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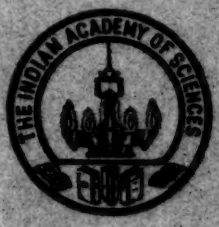

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ON THE THEORY OF THE ELASTICITY OF CRYSTALS

By Sir C. V. Raman and K. S. Viswanathan
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1. Introduction

The branch of mathematical physics known as the theory of the elasticity of solids is based on certain notions regarding elastic stresses and strains which have been accepted doctrine for many years. It is therefore rather surprising to find that those notions are not sustainable and that the theory based on them has to be laid aside in favour of a stricter formulation. The need for such revision was broadly indicated in a recent publication in these *Proceedings* by the present authors (1955); but in view of the importance of the matter, the present paper is prefaced by a clearer and more precise exposition of the necessity for a revision of the classical theory.

Our recent paper dealt with the case of isotropic solids in a formal manner, considering them as homogeneous substances exhibiting the highest possible symmetry in their elastic properties. Usually, however, the so-called isotropic solids are merely polycrystalline aggregates, and a discussion of their elastic behaviour should therefore properly be based on a consideration of the nature and properties of such aggregates. This is a task which we hope to be able to address ourselves in the not-too-distant future. In the present paper we shall consider the case of truly homogeneous but anisotropic solids, in other words, crystals. The subject will be dealt with from the phenomenological standpoint since this proves to be entirely adequate. We may remark, however, that the conclusions reached are in complete accord with the results of the atomistic approach to the theory of elasticity as developed both from the static and dynamic standpoints in a paper by one of us (Viswanathan, 1954) and illustrated by a detailed discussion of a particular case of great interest, *viz.*, diamond.

2. The Physical Characters of Elastic Stress and Strain

A solid body may be defined as a material in which the volume elements retain their relative positions and orientations alike when the solid is at rest and when it is in a state of movement, translatory or rotatory, as the case may be. Elastic stresses and strains arise when the situation thus described is departed from to ever so small an extent. Hence, it is evident

that the theory of elasticity is concerned with changes in the relative positions and/or the relative orientations of the volume elements of the solid, in other words, with linear displacements and/or angular movements of the volume elements with respect to their neighbours. This is illustrated by the familiar examples of a straight bar which is stretched or bent or twisted by the application of appropriate external stresses. From the general considerations indicated above as well as from the particular examples mentioned, it is clear that only in very special cases would elastic strains be such that a straight line drawn through the solid in any direction in the unstrained condition remains straight in the strained state, suffering only elongations or contractions. In the general case, and inevitably so when the strains involve differential rotations, a straight line in the unstrained condition would be curved in the strained state, and such curvature cannot possibly be ignored in the theory. Hence, it is clear that we have, in general, to consider strains and stresses which are heterogeneous, in other words, strains and stresses whose specifications vary from point to point within the solid. These variations necessarily enter into the equations of equilibrium in the static state and into the equations of motion in dynamic behaviour.

3. ANALYTICAL SPECIFICATION OF STRESSES AND STRAINS

The mathematical theory of elasticity proceeds on the basis that the strains and stresses in the interior of the solid can be expressed in terms of the movements of the smallest possible elements of volume into which it can be imagined to be subdivided and of the forces acting on them. If the volume elements be small enough, their movements can be described completely in terms of the three positional co-ordinates of each element and their variations. Likewise, when the elements of volume are small enough, the interactions between each element and its neighbours can be expressed in terms of tractive forces alone, it being then clearly unnecessary to introduce anything in the nature of couples or torques. On the basis of these ideas, the state of strain in the solid at any given point can be expressed by resolving the displacement of the elementary volume originally located at such point along three mutually perpendicular directions and differentiating these three components of displacement again along each of the three axes in turn. We thus obtain the nine components of the strain tensor. Likewise, for specifying the state of stress to which the volume element is subject, we consider the tractive forces acting on an infinitesimal area drawn respectively normal to the three co-ordinate planes in turn at the position of the element and then again resolve these tractive forces along each of the three co-ordinate axes. We thus obtain the nine components of the stress tensor,

It is evident that this method of representation of the stresses and strains uniquely defines the state of the solid at any point and also enables us to determine whether the element of volume would or would not remain in equilibrium. If the components of stress do not vary along any of the three axes, the element would necessarily remain at rest. If, on the other hand, the stress components vary, their differential coefficients along the normals to the planes on which they act gives us a measure of the forces on the volume element in their respective directions. Adding up the three forces along each axis thus evaluated and putting their sums separately equal to zero, we obtain the conditions of equilibrium.

The well-known and familiar treatments given in the standard treatises proceed on the basis that the components of the strain and stress tensors are both reducible in number from nine to six. The arguments on which the reduction in number from nine to six of the components of strain is based may be summarised by the statement that the elastic strains can be separated into what are called " pure strains " and " rotations," and that the latter can be ignored. That this argument is unsustainable will be evident at once from the remarks made in the foregoing section regarding the physical nature of elastic strains. We have, in general, to take account of both differential displacements and differential rotations and it is therefore not permissible to eliminate the rotational parts of the strain, these being physically quite as real as the irrotational parts.

The arguments justifying the reduction in the number of the independent components of stress from nine to six are based upon the idea that equilibrium would be possible only if the angular momenta of the tractions taken about each of the three co-ordinate axes in turn cancel each other out. That this idea is misconceived will be evident from the remarks already made earlier regarding the conditions necessary for equilibrium. In the case of homogeneous strains, the tractive forces acting on each volume element necessarily balance each other. In the case of heterogeneous strains, the conditions of equilibrium can be expressed in terms of the differential coefficients of the stress components along the normals to the planes on which they act, as already explained. In either case, if the equilibrium conditions for each volume element of the solid are satisfied, then the solid as a whole necessarily remains in equilibrium; *vice versa*, if the external stresses acting on the solid are such that it remains as a whole in equilibrium, the elastic stresses would everywhere necessarily be such as to ensure equilibrium of the individual volume elements. It follows that no general relations connecting the magnitude of the tensor components and enabling their number

to be reduced from nine to six can be derived from considerations based on the conditions for equilibrium.

We may summarise our conclusions by stating that neither the reduction of the strain components nor the reduction of the stress components in number from nine to six has any theoretical justification; a correct and complete theory of elasticity has necessarily to take all the nine components of the stress and strain tensors into consideration.

4. THE STRESS–STRAIN RELATIONSHIPS

Writing the nine components of the strain tensor as

$$u_{xx}\ u_{yy}\ u_{zz}\ u_{yz}\ u_{zy}\ u_{zx}\ u_{xz}\ u_{xy}\ u_{yx}$$

$$u_1\ \ u_2\ \ u_3\ \ u_4\ \ u_5\ \ u_6\ \ u_7\ \ u_8\ \ u_9$$

and likewise the nine components of the stress tensor as

$$\mathrm{T}_{xx}\ \mathrm{T}_{yy}\ \mathrm{T}_{zz}\ \mathrm{T}_{yz}\ \mathrm{T}_{zy}\ \mathrm{T}_{zx}\ \mathrm{T}_{xz}\ \mathrm{T}_{xy}\ \mathrm{T}_{yx}$$

$$\mathrm{T}_1\ \ \mathrm{T}_2\ \ \mathrm{T}_3\ \ \mathrm{T}_4\ \ \mathrm{T}_5\ \ \mathrm{T}_6\ \ \mathrm{T}_7\ \ \mathrm{T}_8\ \ \mathrm{T}_9$$

the stress-strain relations can be expressed in the general form

$$\mathrm{T}_m = \sum_{n=1}^{9} d_{mn}\, u_n \qquad (m = 1,\ 2,\ldots.9) \qquad (1)$$

and involve *81* constants. Here the constant d_{mn} relates the stress T_m to the strain u_n and is the ratio of the two for a deformation in which all components other than u_n vanish.

The *81* constants figuring in (1) are not all independent, but reduce in the first instance to forty-five for all solids in view of the relations

$$d_{mn} = d_{nm} \qquad (m,\ n = 1,\ 2\ldots.9) \qquad (2)$$

The above relations follow from the well-known theorem of reciprocity relating forces and the corresponding displacements of dynamical systems. The reciprocity relations further enable us to write down the expression for the deformation energy per unit volume in the neighbourhood of any point and this is given by

$$\mathrm{U} = \tfrac{1}{2} \sum_{m=1}^{9} \mathrm{T}_m\, u_m$$

or

$$2\mathrm{U} = \sum_m \sum_n d_{mn}\, u_m\, u_n \qquad (3)$$

Thus in the general case of a completely anisotropic solid, we have forty-five elastic constants instead of the *21* contemplated by the classical theory.

TABLE I

Crystal System	Point Group	No. of Elastic Constants	
		I	II
Triclinic	All	21	45
Monoclinic	All	13	25
Orthorhombic	All	9	15
Tetragonal	C_4 (4) S_4 ($\bar{4}$) C_{4h}($4/m$) ..	7	13
	D_4 (422) C_{4v}($4mm$) $S_{4v}=D_{2d}$ ($\bar{4}2m$) D_{4h} ($4/m2/m2/m$)	6	9
Trigonal	C_3 (3) S_6 ($\bar{3}$) ..	7	15
	D_3 (32) C_{3v} ($3m$) D_{3d} ($\bar{3}2/m$) ..	6	10
Hexagonal	C_6 (6) C_{3h} ($\bar{6}$) C_{6h} ($6/m$) ..	5	11
	D_6 (622) C_{6v} ($6mm$) D_{3h} ($\bar{6}m2$) D_{6h} ($6/m2/m2/m$)	5	8
Cubic	T (23) T_h ($2/m\bar{3}$) ..	3	5
	O (432) T_d ($\bar{4}3m$) O_h ($4/m\bar{3}2/m$) ..	3	4

The number of independent elastic constants which is forty-five for a completely anisotropic solid diminishes in the case of solids possessing the various elements of symmetry characteristic of the different crystal classes, coming down to four for crystals of the classes T_d, O and O_h. The *number* of surviving constants in each symmetry class can be computed in an elegant fashion by adopting the group-theoretical method developed by Bhagavantam (1949). One is concerned in the present case with a linear relationship between nine stress components and nine strain components, the constants of proportionality being the elastic constants (matrix d_{mn}). Further, the elements of the "elastic constants 9 by 9 matrix" satisfy the relation $d_{mn} = d_{nm}$. With these restrictions, the transformation matrix for the elastic constants can be written out and the corresponding character can be deduced. This comes out as

$$\chi_j'(\mathrm{R}) = 16c^4 \pm 16c^3 + 8c^2 \pm 4c + 1 \qquad (4)$$

where $c = \cos\phi$, R is a symmetry operation and ϕ, the rotation. The *plus* sign is used for proper rotations, and *minus* for an improper one. The corresponding character for the 21-constant theory is

$$\chi_j'(\mathrm{R}) = 16c^4 \pm 8c^3 - 4c^2 + 1 \qquad (5)$$

Table I gives the number of independent constants according to the two formulæ for each symmetry class, while the constants that survive and those that vanish are exhibited in detail for the various cases in Tables II to XII. A comparison of these tables amongst themselves will enable the reader to realise how the existence of common symmetry elements results in the appearance of common features in the Tables of elastic constants. For example, all the twenty constants that vanish for monoclinic crystals also

TABLE II

Triclinic (C_1, C_i)

d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	d_{16}	d_{17}	d_{18}	d_{19}
	d_{22}	d_{23}	d_{24}	d_{25}	d_{26}	d_{27}	d_{28}	d_{29}
		d_{33}	d_{34}	d_{35}	d_{36}	d_{37}	d_{38}	d_{39}
			d_{44}	d_{45}	d_{46}	d_{47}	d_{48}	d_{49}
				d_{55}	d_{56}	d_{57}	d_{58}	d_{59}
					d_{66}	d_{67}	d_{68}	d_{69}
						d_{77}	d_{78}	d_{79}
45 constants							d_{88}	d_{89}
								d_{99}

TABLE III

Monoclinic (C_s, C_2, C_{2h})—diad axis $\parallel z$, plane of reflection $\perp$ to z

d_{11}	d_{12}	d_{13}	0	0	0	0	d_{18}	d_{19}
	d_{22}	d_{23}	0	0	0	0	d_{28}	d_{29}
		d_{33}	0	0	0	0	d_{38}	d_{39}
			d_{44}	d_{45}	d_{46}	d_{47}	0	0
				d_{55}	d_{56}	d_{57}	0	0
					d_{66}	d_{67}	0	0
						d_{77}	0	0
							d_{88}	d_{89}
								d_{99}

25 constants

TABLE IV

Orthorhombic (C_{2v}, D_2, D_{2h})

d_{11}	d_{12}	d_{13}	0	0	0	0	0	0
	d_{22}	d_{23}	0	0	0	0	0	0
		d_{33}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{55}	0	0	0	0
					d_{66}	d_{67}	0	0
						d_{77}	0	0
							d_{88}	d_{89}
								d_{99}

15 constants

TABLE V

Tetragonal (C_4, S_4, C_{4h})—tetrad axis $\parallel z$

d_{11}	d_{12}	d_{13}	0	0	0	0	d_{18}	d_{19}
	d_{11}	d_{13}	0	0	0	0	$-d_{19}$	$-d_{18}$
		d_{33}	0	0	0	0	d_{38}	$-d_{38}$
			d_{44}	d_{45}	d_{46}	0	0	0
				d_{55}	0	$-d_{46}$	0	0
					d_{55}	d_{45}	0	0
						d_{44}	0	0
							d_{88}	d_{89}
								d_{88}

13 constants

TABLE VI

Tetragonal (C_{4v}, S_{4v}, D_4, D_{4h})—tetrad axis $\| z$

d_{11}	d_{12}	d_{13}	0	0	0	0	0	0
	d_{11}	d_{13}	0	0	0	0	0	0
		d_{33}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{55}	0	0	0	0
					d_{55}	d_{45}	0	0
						d_{44}	0	0
							d_{88}	d_{89}
								d_{88}

9 constants

TABLE VII

Trigonal (C_3, S_6)—triad axis $\| z$

d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	d_{16}	d_{17}	d_{18}	$-d_{18}$
	d_{11}	d_{13}	$-d_{14}$	$-d_{15}$	$-d_{16}$	$-d_{17}$	d_{18}	$-d_{18}$
		d_{33}	0	0	0	0	d_{38}	$-d_{38}$
			d_{44}	d_{45}	d_{46}	0	d_{17}	$-d_{17}$
				d_{55}	0	$-d_{46}$	$-d_{16}$	$-d_{16}$
					d_{44}	d_{45}	d_{15}	d_{15}
						d_{55}	d_{14}	d_{14}
							d_{88}	d_{89}
								d_{88}

$d_{88}=d_{11}-d_{12}-d_{89}$

15 constants

TABLE VIII

Trigonal (D_3, D_{3d}, C_{3v})—triad axis $\| z$

d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	0	0	0	0
	d_{11}	d_{13}	$-d_{14}$	$-d_{15}$	0	0	0	0
		d_{33}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{55}	0	0	0	0
					d_{44}	d_{45}	d_{15}	d_{15}
						d_{55}	d_{14}	d_{14}
							d_{88}	d_{89}
								d_{88}

$d_{88}=d_{11}-d_{12}-d_{89}$

10 constants

TABLE IX

Hexagonal (C_{3h}, C_6, C_{6h})—hexad axis $\parallel z$

d_{11}	d_{12}	d_{13}	0	0	0	0	d_{18}	$-d_{18}$
	d_{11}	d_{13}	0	0	0	0	d_{18}	$-d_{18}$
		d_{33}	0	0	0	0	d_{38}	$-d_{38}$
			d_{44}	d_{45}	d_{46}	0	0	0
				d_{55}	0	$-d_{46}$	0	0
$d_{88}=d_{11}-d_{12}-d_{89}$					d_{44}	d_{45}	0	0
11 constants						d_{55}	0	0
							d_{88}	d_{89}
								d_{88}

TABLE X

Hexagonal (D_{3h}, C_{6v}, D_6, D_{6h})—hexad axis $\parallel z$

d_{11}	d_{12}	d_{13}	0	0	0	0	0	0
	d_{11}	d_{13}	0	0	0	0	0	0
		d_{33}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{55}	0	0	0	0
$d_{88}=d_{11}-d_{12}-d_{89}$					d_{44}	d_{45}	0	0
8 constants						d_{55}	0	0
							d_{88}	d_{89}
								d_{88}

TABLE XI

Cubic (T, T_h)

d_{11}	d_{12}	d_{12}	0	0	0	0	0	0
	d_{11}	d_{12}	0	0	0	0	0	0
		d_{11}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{55}	0	0	0	0
					d_{44}	d_{45}	0	0
5 constants						d_{55}	0	0
							d_{44}	d_{45}
								d_{55}

TABLE XII

Cubic (T_d, O, O_h)

d_{11}	d_{12}	d_{12}	0	0	0	0	0	0
	d_{11}	d_{12}	0	0	0	0	0	0
		d_{11}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{44}	0	0	0	0
					d_{44}	d_{45}	0	0
4 constants						d_{44}	0	0
							d_{44}	d_{45}
								d_{44}

disappear in the orthorhombic, tetragonal and cubic systems. Likewise, all the thirty constants that vanish for orthorhombic crystals vanish also for those tetragonal crystals which possess three mutually perpendicular diad axes and for all cubic crystals. A noteworthy feature is that the cubic crystals which exhibit a four-fold axis of symmetry have only four different elastic constants, whereas those cubic crystals that do not exhibit this feature have five constants different from each other.

5. WAVE-PROPAGATION IN CRYSTALS

The general equations of motion of an elastic solid are given by

$$\begin{aligned} \rho \frac{\partial^2 u_x}{\partial t^2} &= \frac{\partial \mathrm{T}_{xx}}{\partial x} + \frac{\partial \mathrm{T}_{xy}}{\partial y} + \frac{\partial \mathrm{T}_{xz}}{\partial z} \\ \rho \frac{\partial^2 u_y}{\partial t^2} &= \frac{\partial \mathrm{T}_{yx}}{\partial x} + \frac{\partial T_{yy}}{\partial y} + \frac{\partial \mathrm{T}_{yz}}{\partial z} \\ \rho \frac{\partial^2 u_z}{\partial t^2} &= \frac{\partial \mathrm{T}_{zx}}{\partial x} + \frac{\partial \mathrm{T}_{zy}}{\partial y} + \frac{\partial \mathrm{T}_{zz}}{\partial z} \end{aligned} \tag{6}$$

where ρ is the density of the medium and $\mathrm{T}_{xx}, \ldots$. are the stress components. If the solid is in equilibrium, the quantities on the left-hand side of these equations, representing the acceleration of an unit volume element, will vanish and we get the conditions of equilibrium of the solid.

To evaluate the velocity of propagation of waves in the solid in any given direction, we first seek solutions of the above equations which are in the form of plane waves of the type

$$\mathbf{u} = \mathbf{A} \exp i \frac{2\pi}{\lambda} (vt - \mathbf{e}\cdot\mathbf{r}) \tag{7}$$

Denoting the components of **A** in the directions of the co-ordinate axes by A^x, A^y, A^z and using once again the four-suffixed symbols for the elastic constants, we now get on substitution of (7) in (6) that

$$\rho v^2 A^x = \sum_{\bar{x}} \sum_{y\bar{y}} d_{x\bar{x}, y\bar{y}}\, e_{\bar{x}}\, e_{\bar{y}}\, A^y \tag{8}$$

and two similar equations for the y and z components.

For a wave progressing in the direction (lmn) equations (8) can alternatively be written as

$$\begin{aligned}
(\lambda_{xx} - \rho v^2) A^x + \lambda_{xy} A^y + \lambda_{xz} A^z &= 0 \\
\lambda_{xy} A^x + (\lambda_{yy} - \rho v^2) A^y + \lambda_{yz} A^z &= 0 \\
\lambda_{xz} A^x + \lambda_{yz} A^y + \lambda_{zz} A^z &= 0
\end{aligned} \tag{9}$$

where λ_{xx}, λ_{xy}.... are given by the scheme

$$\begin{pmatrix} \lambda_{xx} \\ \lambda_{yy} \\ \lambda_{zz} \\ \lambda_{yz} \\ \lambda_{zx} \\ \lambda_{xy} \end{pmatrix} = \begin{pmatrix} d_{11} & d_{88} & d_{77} & 2d_{78} & 2d_{17} & 2d_{18} \\ d_{99} & d_{22} & d_{44} & 2d_{24} & 2d_{49} & 2d_{29} \\ d_{66} & d_{55} & d_{33} & 2d_{35} & 2d_{36} & 2d_{56} \\ d_{69} & d_{25} & d_{34} & (d_{23}+d_{45}) & (d_{39}+d_{46}) & (d_{59}+d_{26}) \\ d_{16} & d_{58} & d_{37} & (d_{57}+d_{38}) & (d_{67}+d_{13}) & (d_{15}+d_{68}) \\ d_{19} & d_{28} & d_{47} & (d_{27}+d_{48}) & (d_{14}+d_{79}) & (d_{12}+d_{89}) \end{pmatrix} \begin{pmatrix} l^2 \\ m^2 \\ n^2 \\ mn \\ nl \\ lm \end{pmatrix}$$

Equations (9) determine the velocities of propagation of the three types of waves in any direction for crystals of the triclinic system which possess no symmetry of structure at all. The number of constants figuring in the wave equations will diminish rapidly as we pass on to crystals of higher symmetry, and become only three for crystals of the T_d, O and O_h classes. We tabulate below the wave equations for the different classes of crystals taking into account of their symmetry.

I. *Monoclinic system* (C_s, C_2, C_{2h})—*diad axis parallel to the z-axis*

$$\begin{aligned}
&(d_{11}l^2 + d_{88}m^2 + d_{77}n^2 + 2d_{18}lm - \rho v^2) A^x + \{d_{19}l^2 + d_{28}m^2 + d_{47}n^2 \\
&\quad + (d_{12} + d_{89}) lm\} A^y + \{(d_{38} + d_{57})\ mn + (d_{13} + d_{67}) nl\} A^z = 0. \\
&\{d_{19}l^2 + d_{28}m^2 + d_{47}n^2 + (d_{12} + d_{89}) lm\} A^x + (d_{99}l^2 + d_{22}m^2 + d_{44}n^2 \\
&\quad + 2d_{29}lm - \rho v^2\} A^y + \{(d_{23} + d_{45}) mn + (d_{39} + d_{46}) nl\} A^z = 0. \\
&\{(d_{38} + d_{57}) mn + (d_{13} + d_{67}) nl\} A^x + \{(d_{23} + d_{45}) mn + (d_{39} + d_{46}) nl\} \\
&\quad A^y + (d_{66}l^2 + d_{55}m^2 + d_{33}n^2 + 2d_{56}lm - \rho v^2) A^z = 0.
\end{aligned}$$

The wave equation contains *twenty* independent constants.

II. *Orthorhombic system* (C_{2v}, D_2, D_{2h}).

$$(d_{11}l^2 + d_{88}m^2 + d_{77}n^2 - \rho v^2)\,A^x + (d_{12} + d_{89})\,lm\,A^y + (d_{13} + d_{67})\,nl\,A^z = 0,$$

$$(d_{12} + d_{89})\,lm\,A^x + (d_{99}\,l^2 + d_{22}m^2 + d_{44}n^2 - \rho v^2)\,A^y + (d_{23} + d_{45})\,mn\,A^z = 0.$$

$$(d_{13} + d_{67})\,nl\,A^x + (d_{23} + d_{45})\,mn\,A^y + (d_{66}l^2 + d_{55}m^2 + d_{33}n^2 - \rho v^2)\,A^z = 0.$$

The wave-equations involve *twelve* distinct constants.

III. *Tetragonal* (C_4, S_4, C_{4h})—*tetrad axis parallel to the z-axis.*

$$\{d_{11}l^2 + d_{88}m^2 + d_{44}n^2 + 2d_{18}\,lm - \rho v^2\}\,A^x + \{d_{19}\,(l^2 - m^2) + (d_{12} + d_{89})\,lm\}\,A^y + \{(d_{38} - d_{46})\,mn + (d_{13} + d_{45})\,nl\}\,A^z = 0$$

$$\{d_{19}\,(l^2 - m^2) + (d_{12} + d_{89})\,lm\}\,A^x + \{d_{88}\,l^2 + d_{11}m^2 + d_{44}n^2 - 2d_{18}lm - \rho v^2\}\,A^y + \{(d_{13} + d_{45})\,mn + (d_{46} - d_{38})\,nl\}\,A^z = 0.$$

$$\{(d_{38} - d_{46})\,mn + (d_{13} + d_{45})\,nl\}\,A^x + \{(d_{13} + d_{45})\,mn + (d_{46} - d_{38})\,nl\}\,A^y + \{d_{55}\,(l^2 + m^2) + d_{33}n^2 - \rho v^2\}\,A^z = 0.$$

The number of independent constants contained in the wave equation is *ten.*

IV. *Tetragonal* (C_{4v}, S_{4v}, D_4, D_{4h})—*tetrad axis parallel to the z-axis.*

$$(d_{11}\,l^2 + d_{88}m^2 + d_{44}n^2 - \rho v^2)\,A^x + (d_{12} + d_{89})\,lm\,A^y + (d_{13} + d_{45})\,nl\,A^z = 0.$$

$$(d_{12} + d_{89})\,lm\,A^x + (d_{88}\,l^2 + d_{11}m^2 + d_{44}n^2 - \rho v^2)\,A^y + (d_{13} + d_{45})\,mn\,A^z = 0.$$

$$(d_{13} + d_{45})\,nl\,A^x + (d_{13} + d_{45})\,mn\,A^y + \{d_{55}\,(l^2 + m^2) + d_{33}\,n^2 - \rho v^2\}\,A^z = 0.$$

The number of independent constants contained in the wave-equation is *seven.*

V. *Trigonal system* (C_3, S_6)—*triad axis parallel to the z-axis.*

$$\{d_{11}l^2 + d_{88}m^2 + d_{55}\,n^2 + 2d_{14}mn + 2d_{17}nl + 2d_{18}lm - \rho v^2\}\,A^x + \{d_{18}\,(m^2 - l^2) - 2d_{17}\,mn + 2d_{14}nl + (d_{12} + d_{89})\,lm\}\,A^y + \{d_{16}\,(l^2 - m^2) + (d_{38} - d_{46})\,mn + (d_{13} + d_{45})\,nl + 2d_{15}lm\}\,A^z = 0,$$

$$\{d_{18}(m^2 - l^2) - 2d_{17}\,mn + 2d_{14}nl + (d_{12} + d_{89})\,lm\}\,A^x + \{d_{88}\,l^2 + d_{11}m^2 + d_{44}n^2 - 2d_{14}mn - 2d_{17}\,nl - 2d_{18}lm - \rho v^2\}\,A^y + \{d_{15}(l^2 - m^2) + (d_{13} + d_{45})\,mn + (d_{46} - d_{38})\,nl - 2d_{16}\,lm\}\,A^z = 0.$$

$$\{d_{16}(l^2 - m^2) + (d_{38} - d_{46})\,mn + (d_{13} + d_{45})\,nl + 2d_{15}\,lm\}\,A^x + \{d_{15}(l^2 - m^2) + (d_{13} + d_{45})\,mn + (d_{46} - d_{38})\,nl - 2d_{16}lm\}\,A^y + \{d_{44}l^2 + d_{55}m^2 + d_{33}n^2 - \rho v^2\}\,A^z = 0$$

where

$$d_{88} = (d_{11} - d_{12} - d_{89})$$

The number of independent constants contained in the wave equations is *twelve*.

VI. *Trigonal* (D_3, D_{3d}, C_{3v})—*triad axis parallel to the z-axis.*

$$\{d_{11}l^2 + d_{88}\,m^2 + d_{55}\,n^2 + 2d_{14}mn - \rho v^2\}\,A^x + \{2d_{14}nl + (d_{12} + d_{89})\,lm\}\,A^y + \{(d_{13} + d_{45})\,nl + 2d_{15}\,lm\}\,A^z = 0.$$

$$\{2d_{14}nl + (d_{12} + d_{89})\,lm\}\,A^x + \{d_{88}l^2 + d_{11}m^2 + d_{44}n^2 - 2d_{14}mn - \rho v^2\}\,A^y + \{d_{15}(l^2 - m^2) + (d_{13} + d_{45})\,mn + d_{46}nl\}\,A^z = 0.$$

$$\{(d_{13} + d_{45})\,nl + 2d_{15}\,lm\}\,A^x + \{d_{15}(l^2 - m^2) + (d_{13} + d_{45})\,mn + d_{46}\,nl\}\,A^y + \{d_{44}l^2 + d_{55}m^2 + d_{33}n^2 - \rho v^2\}\,A^z = 0.$$

where

$$d_{88} = (d_{11} - d_{12} - d_{89})$$

The number of independent constants contained in the wave equations is *eight*.

VII. *Hexagonal* (C_{3h}, C_6, C_{6h})—*hexad axis parallel to the z-axis.*

$$\{d_{11}l^2 + d_{88}\,m^2 + d_{55}\,n^2 + 2d_{18}\,lm - \rho v^2\}\,A^x + \{d_{18}(m^2 - l^2) + (d_{12} + d_{89})\,lm\}\,A^y + \{(d_{38} - d_{46})\,mn + (d_{13} + d_{45})\,nl\}\,A^z = 0.$$

$$\{d_{18}(m^2 - l^2) + (d_{12} + d_{89})\,lm\}\,A^x + \{d_{88}\,l^2 + d_{11}m^2 + d_{44}n^2 - 2d_{18}\,lm - \rho v^2\}\,A^y + \{(d_{13} + d_{45})\,mn + (d_{46} - d_{38})\,nl\}\,A^z = 0.$$

$$\{(d_{38} - d_{46})\,mn + (d_{13} + d_{45})\,nl\}\,A^x + \{(d_{13} + d_{45})\,mn + (d_{46} - d_{38})\,nl\}\,A^y + \{d_{44}l^2 + d_{55}\,m^2 + d_{33}\,n^2 - \rho v^2\}\,A^z = 0.$$

where

$$d_{88} = (d_{11} - d_{12} - d_{89})$$

The number of independent constants contained in the wave equations is *eight*.

VIII. *Hexagonal* (D_{3h}, C_{6v}, D_6, D_{6h})—*hexad axis parallel to the z-axis.*

$$(d_{11}l^2 + d_{88}m^2 + d_{55}n^2 - \rho v^2)\,A^x + (d_{12} + d_{89})\,lm\,A^y + (d_{13} + d_{45})\,nl\,A^z = 0.$$

$$(d_{12} + d_{89})\,lm\,A^x + (d_{88}l^2 + d_{11}m^2 + d_{44}n^2 - \rho v^2)\,A^y + (d_{13} + d_{45})\,mn\,A^z = 0.$$

$$(d_{13} + d_{45})\,(nl\,A^x + mn\,A^y) + (d_{44}l^2 + d_{55}m^2 + d_{33}n^2 - \rho v^2)\,A^z = 0.$$

Here again the relation

$$d_{88} = d_{11} - d_{12} - d_{89}$$

characteristic of crystals of the trigonal systems subsists, and number of independent constants appearing in the wave equations is *six*.

IX. *Cubic* (T *and* T_h).

$$(d_{11}l^2 + d_{44}m^2 + d_{55}n^2 - \rho v^2)\,A^x + (d_{12} + d_{45})\,(lm\,A^y + nl\,A^z) = 0.$$

$$(d_{12} + d_{45})\,lm\,A^x + (d_{11}m^2 + d_{44}n^2 + d_{55}l^2 - \rho v^2)\,A^y + (d_{12} + d_{45})\,mn\,A^z = 0.$$

$$(d_{12} + d_{45})\,(nl\,A^x + mn\,A^y) + (d_{11}n^2 + d_{44}l^2 + d_{55}m^2 - \rho v^2)\,A^z = 0.$$

The number of independent elastic constants appearing in the wave equations is *four*.

X. *Cubic* (T_d, O *and* D_h).

$$\{d_{11}l^2 + d_{44}(m^2 + n^2) - \rho v^2\}\,A^x + (d_{12} + d_{45})\,\{lm\,A^y + nl\,A^z) = 0\}.$$

$$(d_{12} + d_{45})\,lm\,A^x + \{d_{11}m^2 + d_{44}(l^2 + m^2) - \rho v^2\}\,A^y + (d_{12} + d_{45})\,mn\,A^z = 0.$$

$$(d_{12} + d_{45})\,\{nl\,A^x + mn\,A^y\} + \{d_{11}l^2 + d_{44}(l^2 + m^2) - \rho v^2\}\,A^z = 0.$$

The number of independent constants appearing in the wave equations is *three*.

6. STATIC DEFORMATION PROBLEMS

Equations (1) express the nine stress components in terms of the nine strain coefficients. One can work out the inverse transformation of (1) and express instead the strain coefficients as linear functions of the stress variables. The strain-stress relations can therefore alternatively be written also as

$$u_m = \sum_{n=1}^{9} D_{mn}\,T_n \qquad (m = 1, 2, \ldots 9) \qquad (10)$$

If Δ_{mn} denotes the co-factor of the element d_{mn} in the determinant of the transformation (1) and Δ = determinant $|d_{mn}|$, then $D_{mn} = (\Delta_{mn}/\Delta)$.

The strain-energy can be expressed purely as a function of the stress coefficients and we have another expression

$$2U = \sum_m \sum_n D_{mn} T_m T_n \tag{11}$$

for the deformation energy which is equivalent to (3).

In the classical theory the nine stress variables are reduced to six by means of the relations $T_{yz} = T_{zy}$; $T_{zx} = T_{xz}$; $T_{xy} = T_{yx}$. The deformation energy of the solid is thus a function of the six stress variables only. Adopting the usual convention of writing T_1', T_2', T_3', T_4', T_5', T_6' for T_{xx}, T_{yy}, T_{zz}, T_{yz} or T_{zy}, T_{zx} or T_{xz}, T_{xy} or T_{yx} respectively, the classical expression (4) for the strain-energy becomes

$$2U_1 = \sum_{m,\, n=1}^{6} s_{mn} T_m' \, T_n' \tag{12}$$

The coefficients s_{mn} occurring in the above expression are the well-known *elastic moduli* of the classical theory. One can obtain formulæ for these moduli in terms of our constants D_{mn} by considering cases of homogeneous stresses for which the relations $T_{yz} = T_{zy}$; $T_{zx} = T_{xz}$; $T_{xy} = T_{yx}$ hold good. Making these substitutions in (11) and comparing the resulting expression with (2), we get $s_{mn} = D_{mn}$ when both m and n are 1, 2, or 3 and relations of the type

$$\begin{aligned} s_{14} &= (D_{14} + D_{15}); \\ s_{44} &= (D_{44} + 2D_{45} + D_{55}); \\ s_{45} &= (D_{46} + D_{47} + D_{56} + D_{57}); \end{aligned} \tag{13}$$

for the other coefficients.

We can now write down the expressions for the compressibility, Young's modulus, and the Poisson's ratio for any crystal in simple terms. In view of the fact that all these moduli are determinable from experiments dealing with purely homogeneous strains, the formulæ for them are not essentially different from the corresponding ones of the classical theory. By following the same methods as those adopted in the latter,[3] we give below the formulæ for these moduli in our present notation.

When the crystal is subjected to a uniform hydrostatic pressure P, we have from the first three of the equations (10)

$$u_1 = (D_{11} + D_{12} + D_{13})\,P$$
$$= (s_{11} + s_{12} + s_{13})\,P \text{ from (13)}$$
$$u_2 = (s_{21} + s_{22} + s_{23})\,P$$
$$u_3 = (s_{31} + s_{32} + s_{33})\,P$$

The linear compressibility modulus in the direction of the x-axis is therefore given by

$$k_x = (P/u_1) = 1/(s_{11} + s_{12} + s_{13}) \tag{14}$$

and the bulk modulus is expressed by the formula

$$k = P/(u_1 + u_2 + u_3) = 1/(s_{11} + s_{22} + s_{33} + 2s_{23} + 2s_{31} + 2s_{12}) \tag{15}$$

If the solid is subjected to a uniform tension T in the direction of the x-axis, obviously $T_1 = T$; $T_2 = T_3 = \ldots T_9 = 0$. Hence it follows from (10) that the Young's modulus in the direction of the x-axis is given by

$$E = T/u_1 = (1/D_{11}) = (1/s_{11}) \tag{16}$$

Similarly the Poisson's ratio in the direction of the y-axis is given by

$$\sigma = -(s_{12}/s_{11}) \tag{17}$$

To write down the expressions for the Young's modulus and Poisson's ratio in any general direction (l, m, n), we require the law of transformation of the strain as well as the stress components when one passes over from one co-ordinate system to another. If the direction cosines of the axes Ox', Oy' Oz' of a new co-ordinate system referred to the original one are (l_1 m_1 n_1), (l_2 m_2 n_2) and (l_3 m_3 n_3) respectively, we have

$$T_{x'x'} = l_1^2 T_{xx} + m_1^2 T_{yy} + n_1^2 T_{zz} + m_1 n_1 (T_{yz} + T_{zy}) + n_1 l_1 (T_{zx} + T_{xz}) + l_1 m_1 (T_{xy} + T_{yx})$$

$$T_{x'y'} = l_1 l_2 T_{xx} + m_1 m_2 T_{yy} + n_1 n_2 T_{zz} + (m_1 n_2 T_{yz} + m_2 n_1 T_{zy}) + (n_1 l_2 T_{zx} + n_2 l_1 T_{xz}) + (l_1 m_2 T_{xy} + l_2 m_1 T_{yx}) \tag{18}$$

$$T_{y'x'} = l_1 l_2 T_{xx} + m_1 m_2 T_{yy} + n_1 n_2 T_{zz} + (m_2 n_1 T_{yz} + m_1 n_2 T_{zy}) + (n_2 l_1 T_{zx} + n_1 l_2 T_{xz}) + (l_2 m_1 T_{xy} + l_1 m_2 T_{yx}$$

$$u_{x'x'} = l_1^2 u_{xx} + m_1^2 u_{yy} + n_1^2 u_{zz} + m_1 n_1 (u_{yz} + u_{zy}) + n_1 l_1 (u_{zx} + u_{xz}) + l_1 m_1 (u_{xy} + u_{yx}) \tag{19}$$

$$u_{x'y'} = l_1 l_2 u_{xx} + m_1 m_2 u_{yy} + n_1 n_2 u_{zz} + (m_1 n_2 u_{yz} + m_2 n_1 u_{zy}) + (n_1 l_2 u_{zx} + n_2 l_1 u_{xz}) + (l_1 m_2 u_{xy} + l_2 m_1 u_{yx})$$

$$u_{y'x'} = l_1 l_2 u_{xx} + m_1 m_2 u_{yy} + n_1 n_2 u_{zz} + (m_2 n_1 u_{yz} + m_1 n_2 u_{zy}) + (n_2 l_1 u_{zx} + n_1 l_2 u_{xz}) + (l_2 m_1 u_{xy} + l_1 m_2 u_{yx})$$

Now, if the solid is subjected to a uniform tension T over the planes $x' = \text{const.}$ of which the normal has direction cosines $(l_1\, m_1\, n_1)$, we get from the transformation rules

$$\mathrm{T}_{xx} = l_1^2\mathrm{T};\ \mathrm{T}_{yy} = m_1^2\mathrm{T};\ \mathrm{T}_{zz} = n_1^2\mathrm{T};\ \mathrm{T}_{yz} = \mathrm{T}_{zy} = m_1n_1\mathrm{T};$$
$$\mathrm{T}_{zx} = \mathrm{T}_{xz} = n_1l_1\mathrm{T};\ \mathrm{T}_{xy} = \mathrm{T}_{yx} = l_1m_1\mathrm{T}$$

Further, $u_{x'x'}$ is given by (19). Hence denoting by $\mathbf{q}_{x'}$ the row vector $(l_1^2\ m_1^2\ n_1^2\ m_1n_1\ n_1l_1\ l_1m_1)$ with six components, we find the expression for the Young's modulus in the direction of the vector $(l_1\, m_1\, n_1)$ as

$$\mathrm{E}_{x'} = 1/\mathbf{q}_{x'}\,\mathrm{S}\,\tilde{\mathbf{q}}_{x'} \tag{20}$$

where S denotes the matrix (s_{mn}). Similarly the Poisson's ratio in the direction of the y'-axis which has direction cosines $(l_2\, m_2\, n_2)$ with respect to O_x, O_y and O_z is given by

$$\sigma_{y'} = -\frac{1}{2\phi}\left[l_2^2\frac{\partial\phi}{\partial l_1^2} + m_2^2\frac{\partial\phi}{\partial m_1^2} + n_2^2\frac{\partial\phi}{\partial n_1^2} + m_2n_2\frac{\partial\phi}{\partial(m_1n_1)} + n_2l_2\frac{\partial\phi}{\partial(n_1l_1)} + l_2m_2\frac{\partial\phi}{\partial(l_1m_1)}\right] \tag{21}$$

where $\phi = \mathbf{q}_{x'}\,\mathrm{S}\tilde{\mathbf{q}}_{x'}$ and the differential coefficients are formed as if these arguments are independent.

It is interesting to note that only twenty-one of the forty-five constants figuring in (10) appear in the above formulæ. As mentioned earlier, this is a consequence of the homogeneity of the strains applied to evaluate these static moduli.

The stresses and strains which appear when elastic materials are subject to torsion or flexure are essentially heterogeneous, and hence in dealing with them, our elastic moduli D_{mn} will appear in combinations other than those which figure in homogeneous deformations. The present theory is quite competent to handle such problems, but to deal with them in detail would carry us far beyond the scope of this paper.

7. Some Concluding Remarks

The main purpose of the present paper has been to establish the necessity for an amendment of the phenomenological theory of elasticity as universally accepted hitherto. Any theory to be acceptable should include in its scope elastic stresses and strains of the most general type and specify them in an analytical form from which the equations of equilibrium in static

problems and the equations of motion in wave-propagation can be written down immediately. These requirements are not met by the present form of the theory but are completely satisfied if all the nine components of stress and strain in the usual tensor formulation are retained. When thus amended, the phenomenological theory is capable of handling all the problems of the subject, including those which arise in its practical applications. The more important of these are considered in detail in the course of the paper and the results are set out explicitly for the different crystal classes so that they could be readily made use of.

As already remarked in the introduction, the phenomenological theory as amended gives results in complete accord with those derived from the atomistic approach to the theory of elasticity of crystals based on the most general scheme of interatomic forces. To discuss the latter further or to give an account of the somewhat confused history of the subject would lie outside the scope of the present paper. A few remarks regarding these matters will however be found in the attached appendix.

SUMMARY

The fundamental aspects of the phenomenological theory of elasticity are critically examined and it is shown that the tensor representation of the elastic strains and stresses in the general case should be in the unsymmetrical form. On this basis, the stress-strain relationships are deduced and tabulated for the different crystal classes. The equations determining the velocities of wave-propagation in different directions are also obtained and tabulated. Static deformation problems are then discussed and it is shown that in the particular case of homogeneous strains, the elastic constants group themselves in linear combinations which are equivalent to the elastic modulii of the theory in its familiar form. In wave-propagation, however, the strains and stresses are heterogeneous and hence all the elastic constants are involved and appear in linear combinations which are different and also larger in number than those which figure in the formulæ for homogeneous deformations. These results are completely in accord with the consequences of the atomistic theory based on interatomic forces of the most general type.

APPENDIX

As is well known, the theory of the elasticity of solids in its present form was initiated by Cauchy who put forth the fundamental idea of expressing elastic stresses and strains in the manner adopted in the phenomenological theory, and also developed the theory on an atomistic basis. Later theorists, notably Green, Stokes and Kelvin retained Cauchy's method of specifying elastic stresses and strains but adopted a purely phenomenological approach. The view advocated by them that a completely ælotropic body would have twenty-one elastic constants and not fifteen as derived by Cauchy received general acceptance.

In a paper published in these *Proceedings* some years ago by one of us (Raman, 1943), a theory of the dynamic behaviour of crystal lattices was developed based on the assumption of interatomic forces of the most general type. In subsequent years, the consequences of that theory was worked out in detail for the case of diamond and confirmed by a series of spectroscopic investigations on the scattering of light, the luminescence and infra-red absorption by that crystal. The high values of the interatomic force-constants disclosed by the spectroscopic behaviour of diamond were evidently related to its exceptional elastic behaviour. In the endeavour to place this relationship on a quantitative basis, a fresh approach was made by one of us (Viswanathan, 1954) to the atomistic theory of the elasticity of crystals, both from the static and dynamic points of view, and some surprising results emerged. Contrary to the assertion made in the papers of Max Born and his collaborators which also finds a place in their recent book (Born and Kun Huang, 1954), no difficulty was encountered in expressing the energy of static deformations in terms of interatomic forces of the most general type. It was found that this expression contained forty-five independent constants, but for homogeneous or irrotational strains they appeared in twenty-one distinct linear combinations. The dynamics of wave-propagation in crystals was also investigated and it was shown that the expressions for the wave-velocity contained the same forty-five constants but in different linear combinations. The work of Born and his school on the dynamic problem was critically examined and it was shown that the assumptions made by them in the attempt to reduce the forty-five constants which appeared in their theory to twenty-one had no theoretical justification.

The results of Born and his school were also contradicted by Laval in some recent publications (1951). More recently still, a series of papers have been published by Le Corre in which Laval's ideas have been further developed. On reading those papers, one obtains the impression that their

author believes the results of the atomistic and phenomenological approaches to differ essentially. For example, in order to account for the non-symmetric character of the stress tensor, internal couples are postulated to balance the differences in the angular momenta. We may remark that there is no room for such a postulate, since the analytical specification of the stresses in terms of the tensor components should itself suffice to describe the state of the solid completely. In the last paper of the series, a statement also appears that an atomistic approach is essential to solve such familiar problems in elasticity as torsion and flexure.

In conclusion, we have to thank Mr. A. K. Ramdas for his help in the preparation of the tables appearing in the paper.

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STUDIES ON DIFFUSION

Part I. Diffusion of Radioactive Matter Through Plates

By U. Aswathanarayana
(*Department of Geology*)
AND
S. Ramamurthy
(*Department of Mathematical Physics, Andhra University, Waltair*)

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Abstract

As a part of an attempt to develop new methods of measurement of diffusion constant of metals and non-metals into minerals using radioactivity techniques, expressions are derived to relate the processes of diffusion and the emission of alpha-particles under three sets of possible experimental conditions. The first case pertains to a plate whose thickness is equal to the characteristic range of the alpha-rays of the radionuclide used. Under the second case is considered a plate thicker than the characteristic range of the alpha-rays in the plate. The third deals with cases wherein the radioactive matter used emits alpha-rays with different ranges less than the thickness of the plate.

Introduction

The problem of diffusion of metals in the solid state has been extensively studied during the last three decades (Mehl, 1936), because of its importance in the industrial operations like the preparation of special alloys and the development of nitriding, chromizing and calorizing, sherardizing and siliconizing and the formation of bi-metal strip and veneering metals. Diffusion data are also essential for studies on crystal physics and the elucidation of phenomena such as annealing, age hardening, plasticity and order-disorder transformations in alloys. Our present state of knowledge on the subject of solid diffusion has recently been reviewed by Barrer (1951).

The voluminous literature on metal diffusion stands in marked contrast to the virtual absence of any systematic work on the measurement of diffusion constants of metals and non-metals in minerals and rocks. The discovery of radioactive isotopes gave a great fillip to self-diffusion studies on metals (Hevesy *et al.*, 1913, 1925, 1929 *a*, *b*, 1932, 1933; Groh and Hevesy,

1920; McKay, 1938; Steigman *et al.*, 1939). The pioneering work of Jensen (1952) on the solid diffusion of radioactive sodium (Na^{22}) in perthite shows tremendous potentialities for further researches on the subject.

The principles of diffusion have been discussed in detail in an earlier communication (Aswathanarayana, 1954). As a part of the long-range programme of theoretical and laboratory investigations on the measurement of diffusion constants, an attempt is made now to derive expressions relating the processes of diffusion and emission of alpha-particles.

General Statement of the Problem

Let A B C D-A′ B′ C′ D′ with dimensions a, b, c (a being the thickness) represent a thin, uniform section of a mineral. A uniform, thin coating of an alpha-emitting radio-nuclide is given to the face A B C D. Let v be the concentration of radioactive matter on that surface. Simultaneously with the above operation, an α-particle detecting device—nuclear emulsion plate suitable for alpha-track radiography—is kept in contact with the face A′ B′ C′ D′ of the thin section. Each radioactive atom undergoing decay acts as a centre of a sphere of radius equal to the range of alpha radiation in the medium. When the sphere intersects the plane of the emulsion, it leaves behind its imprint in the form of an image (Yagoda, 1949). The number of alpha-particles emerging from the lower face A′ B′ C′ D′ and getting recorded on the nuclear emulsion plate is a function of (1) the concentration (v) of radioactive matter on the face A B C D, which determines the rate of production of alpha-particles, (2) the characteristic range (ρ) of the alpha-particles of the radioactive nuclide in the mineral and (3) the thickness of the plate (a). With time, a part of the material of the radioactive nuclide diffuses into the mineral and this results in a larger number of alpha-rays emerging from the face A′ B′ C′ D′ of the mineral section and getting recorded on the plate. Thus from a knowledge of (1) the range (ρ) of alpha-particles of the radioactive nuclide, (2) the concentration (v) of radioactive matter on the plate and (3) the number of alpha-particles (N) recorded on the plate after a time T, it is possible to determine the diffusion constant (D).

Mathematical Treatment

The following assumptions are made in this context:—

(i) The diffusion of radioactive matter in a mineral is governed by laws analogous to laws of conduction of heat in a solid and (ii) the mineral exhibits diffusion isotropy.

The concentration $v\ (x,\ y,\ z,\ t)$ is governed by

$$\frac{\partial v}{\partial t} = \mathrm{D}\nabla^2 v\ .$$

The experimental conditions may be taken as equivalent to the diffusion of matter in a rectangular slab of thicknesses a, b, c, where a is the distance between the plane on which radioactive matter has been spread and the opposite plane (which is in contact with the nuclear emulsion plate).

The boundary conditions are:

$$\begin{aligned} &\text{at} \quad x = 0 \qquad v = v_1 \\ &\left.\begin{aligned} x &= a \\ y &= 0 \\ y &= b \\ z &= 0 \\ z &= c \end{aligned}\right\} \quad v = 0 \\ &\text{at} \quad t = 0 \qquad v = 0. \end{aligned}$$

Then v can be written as the sum of two terms U and W (say)—U being a function of x, y, z alone and W, a function of x, y, z, t (Carslaw and Jaeger, 1947, pp. 18–19, 165).

Concentration $v = v\ (x, y, z, t)$

$$v\ (x, y, z, t) = \frac{16v_1}{\pi^2} \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \frac{\sinh \alpha\ (a - x) \sin \dfrac{(2p+1)\pi y}{b} \sin \dfrac{(2q+1)\pi z}{c}}{(2p+1)\ (2q+1) \sinh \alpha a}$$

$$- \frac{32v_1}{\pi} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \sum_{l=1}^{\infty}{}' \frac{le^{-\mathrm{D}a^2_{l,\,m,\,n}\,t} \sin \dfrac{l\pi x}{a} \sin \dfrac{m\pi y}{b} \sin \dfrac{n\pi z}{c}}{mn \left\{\pi^2 l^2 + a^2 \left(\dfrac{m^2\pi^2}{b^2} + \dfrac{n^2\pi^2}{c^2}\right)\right\} \sinh a \sqrt{\dfrac{m^2\pi^2}{b^2} + \dfrac{n^2\pi^2}{c^2}}}$$

where

$$a^2 = \frac{(2p+1)\pi^2}{b^2} + \frac{(2q+1)\pi^2}{c^2}$$

$$a^2_{l,m,n} = \pi^2 \left(\frac{l^2}{a^2} + \frac{m^2}{b^2} + \frac{n^2}{c^2}\right).$$

Case I.—The following experimental conditions are assumed in this case: (i) the thickness (a) of the slab is equal to the range (ρ) of the α-particles of the radio-nuclide, (ii) the α-rays are mono-energetic or in other

words, they all have a characteristic specific range (ρ) in the mineral, (iii) the radioactive matter has been spread on the mineral surface uniformly and (iv) the nuclear emulsion plate is in contact with the lower side of the mineral plate simultaneously with the spreading of radioactive matter on the upper surface.

The number of α-particles emitted between the time instants 0 and T is given by

$$N = \int_0^T dt \int_0^c dz \int_0^b dy \int_0^a v\lambda dx$$

where λ is the fraction of radioactive matter that disintegrates per second.

Putting

$$A = \frac{64\, v_1 bc}{\pi^4 a_0 \sinh(a_0 a)} [\cosh(a_0 a) - 1],$$

$$B = \frac{256\, v_1 ab^3c^3}{\pi^6 \{b^2c^2 + a^2(b^2 + c^2)\} \sinh \frac{\pi a}{bc} \sqrt{b^2 + c^2}},$$

$$a_0 = \pi \sqrt{\frac{1}{b^2} + \frac{1}{c^2}},$$

$$a = \pi \sqrt{\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}},$$

we get

$$\frac{N}{\lambda} = (A - B)\, T + \frac{B\alpha^2 T^2}{2} D \qquad \text{(approximately)},$$

taking into account the terms in v with $p = q = 0$, and $l = m = n = 1$. From this equation D can be calculated.

Case II.—In the second case, the following experimental conditions are assumed: (i) The thickness (a) of the plate is larger than the range (ρ) of the alpha-particles of the radio-nuclide in the mineral, (ii) the alpha-particles are mono-energetic, (iii) spreading of the radioactive matter on the mineral face A B C D is uniform and (iv) the nuclear emulsion plate is in position by the time radioactive matter reached $x = a - \rho$ plane.

$$\frac{N}{\lambda} = \int_\tau^T dt \int_0^c dz \int_0^b dy \int_{a-\rho}^a v dx$$

where τ is the time taken by the readioactive matter to reach the plane $x = a - \rho$. It is given by

$$D\tau = \frac{1}{a^2}\log_e \frac{\pi \left\{1 + a^2\left(\frac{1}{b^2} + \frac{1}{c^2}\right)\right\} \sinh \pi a \sqrt{\frac{1}{b^2} + \frac{1}{c^2}} \sinh (\alpha_0 \rho)}{2 \sinh (\alpha_0 a) \sin \pi \left(1 - \frac{\rho}{a}\right)}$$

approximately.

Putting

$$A' = \frac{64 v_1 bc}{\pi^4 \sinh (\alpha_0 a)} [\cosh (\alpha_0 \rho) - 1],$$

$$\beta = \frac{B}{4}\left\{1 + \cos \pi \left(1 - \frac{\rho}{a}\right)\right\} \alpha^2 (T^2 - \tau^2),$$

$$\gamma = A' - \frac{B}{2}\left\{1 + \cos \pi \left(1 - \frac{\rho}{a}\right)\right\}$$

(β, α, α_0 the same as above in Case I), we get

$$\frac{N}{\lambda} = \gamma (T - \tau) + \beta D \qquad \text{(approximately)},$$

whence D can be calculated.

Case III.—This case is similar to the second case but for the assumption that the alpha-particles emitted by the radioactive matter are not monoenergetic, *i.e.*, they have got several ranges as different from a single range considered under the second case.

Let ρ, ρ', $\rho'' \ldots . \rho^{(n)}$ be the ranges of α-particles emitted by the radioactive matter. Let $\rho < \rho' < \rho'' \ldots . \rho^{(n)} < a$. Let $\tau^{(r)}$ be the time taken by the radioactive matter to penetrate to such depth that radiations from it of range $\rho^{(r)}$ can influence the photographic plate. Let T be the time that has elapsed upto the removal of the photographic plate.

Then

$$\frac{N}{\lambda} = \int_{\tau}^{T} dt \int_{0}^{c} dz \int_{0}^{b} dy \int_{a-\rho}^{a} v dx$$

$$+ \int_{\tau'}^{T} dt \int_{0}^{c} dz \int_{0}^{b} dy \int_{a-\rho'}^{a} v dx$$

$$+ \ldots\ldots\ldots\ldots\ldots\ldots$$

$$+ \int_{\tau^{(n)}}^{T} dt \int_{0}^{c} dz \int_{0}^{b} dy \int_{a-\rho^{(n)}}^{a} v dx,$$

Let the values of β and γ in Case II be termed as $\beta^{(s)}$ and $\gamma^{(s)}$ when $\rho = \rho^{(s)}$ and $\tau = \tau^{(s)}$. Then

$$\frac{N}{\lambda} = \sum_s \gamma_s (T - \tau_s) + D \sum_s \beta_s \quad \text{(approximately).}$$

From this formula D can be calculated.

Further investigations are proceeding.

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RAMAN SPECTRA OF NICKEL SULPHATE CRYSTALS

By D. Krishnamurti

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1. Introduction

Nickel sulphate crystallizes from solution at room temperature (30° C.) as $NiSO_4.7H_2O$ in the orthorhombic system. At about 35° C it crystallizes as $NiSO_4.6H_2O$ in the tetragonal system, while at about 60° C. it crystallizes as $NiSO_4.6H_2O$ but in the monoclinic system. The complete Raman spectrum of crystalline nickel sulphate has not so far been reported since the λ 4358 and λ 4046 radiations of the mercury arc ordinarily employed are absorbed. Nisi (1930) using the group of lines at λ 3126 in the mercury arc spectrum has reported in the case of $NiSO_4.7H_2O$ the principal sulphate frequency of shift 985 cm.$^{-1}$ and two water bands at 3209 and 3432 cm.$^{-1}$

The absorption in the near ultraviolet for nickel sulphate lies at λ 3850 and the crystals are transparent to radiations of shorter wavelengths over a wide range in the ultraviolet. The present paper reports the results of an investigation with the orthorhombic and tetragonal crystals using the resonance radiation λ 2536·5 of the mercury arc for exciting the Raman effect.

2. Experimental Details

The crystals of $NiSO_4.7H_2O$ and $NiSO_4.6H_2O$ were grown by the method of slow evaporation, the latter at a temperature of 35° C. in a thermostat. The crystals of $NiSO_4.6H_2O$ were of a deeper green in colour than those of $NiSO_4.7H_2O$. The biaxial nature of the interference figures in the case of $NiSO_4.7H_2O$ and the uniaxial nature of the figures of $NiSO_4.6H_2O$ observed under the polarising microscope confirmed their respective identification from depth of colour and external form. The crystals of $NiSO_4.7H_2O$ were in the form of rectangular tablets of size 20 mm. $\times$ 10 mm. $\times$ 2 mm. The crystals of $NiSO_4.6H_2O$ which were pyramidal in form were rather small. Since both the crystals were efflorescent, a thin film of glycerine was put over them to reduce the rate of efflorescence. However, the crystals of $NiSO_4.7H_2O$ deteriorated rapidly and fresh crystals had to be used frequently.

The Raman spectra were recorded with a Hilger medium quartz spectrograph having a dispersion of 140 cm.$^{-1}$ per mm. in the λ2536·5 region. A

water-cooled magnet controlled quartz mercury arc served as an intense source of λ 2536·5. The crystals were placed near the arc and the scattered radiations were focussed on the slit of the spectrograph with a quartz condenser. The scattered resonance radiation was filtered out by the mercury vapour inside the spectrograph. With a slit width of 0·04–0·05 mm., exposures of the order of ten hours were given to obtain reasonably intense spectrograms.

3. RESULTS

Figs. (1) and (2) in the accompanying Plate reproduce the spectra obtained with $NiSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ respectively. The lowermost part of the spectrum in Fig. 2 which is very intense due to parasitic light helps to identify the lines of the mercury arc.

An examination of the spectra of the two crystals reveals the following features: (1) The low frequency spectra of these crystals are faint and

TABLE I

Frequency Shifts in cm.$^{-1}$

	$NiSO_4 \cdot 7H_2O$	$NiSO_4 \cdot 6H_2O$
Lattice Oscillations	~ 75 v.w. ~ 110 v.w. ~ 156 w. 210 m. 255 b.m.	 210 m. 236–69 b.m.
ν_2	400 w. 444 s. 465 s.	 440 s. 469 s.
ν_3	620 ?	620 ?
ν_1	986 v.s.	988 v.s.
ν_4	1060 b.s. 1098 b.m. 1138 b.s. ~1165 v.w.	 1092 b.s. 1133 b.s.
Water Bands	~3282 v.s. ~3438 v.s.	~3257 v.s. ~3439 v.s.

s., Strong; w., weak; v.s., very strong; v.w., very weak; m., medium; b., broad.

~ value of the frequency shift estimated from the relative position of the line with respect to the neighbouring iron arc lines.

diffuse. (2) The frequency shifts due to the oscillations of the sulphate ions in the two crystals are different in the two cases. It may be noticed that the splitting of the doubly degenerate oscillation at 450 cm.$^{-1}$ is larger in the case of $NiSO_4 \cdot 6H_2O$ than in the case of $NiSO_4 \cdot 7H_2O$. Measurements indicate that the non-degenerate oscillation has a frequency shift of 986 cm.$^{-1}$ in the case of $NiSO_4 \cdot 7H_2O$, while in the case of $NiSO_4 \cdot 6H_2O$ it has a shift of 988 cm.$^{-1}$ It will also be noticed that the triply degenerate oscillation at 1100 cm.$^{-1}$ has split into more components in the case of $NiSO_4 \cdot 7H_2O$ which is of lower symmetry than $NiSO_4 \cdot 6H_2O$. The water bands also show differences in their structure in the two cases.

Table I gives the frequency shifts observed in the two cases. The frequency shifts of some of the lines which were faint and diffuse could only be approximately estimated. The sulphate ion frequency of shift about 620 cm.$^{-1}$ could not be unambiguously observed owing to the proximity of the intense mercury line at λ 2576.

4. Discussion

$NiSO_4 \cdot 7H_2O$ has been assigned to the space group $P\,2_12_12_1\,(D_2^4)$ of the enantiomorphous hemihedral class of the orthorhombic system, whereas $NiSO_4 \cdot 6H_2O$ has been assigned to the space group $P\,4_12_12\,(D_4^4)$ of the enantiomorphous hemihedral class of the tetragonal system. (Beevers and Schwartz, 1935; Beevers and Lipson, 1932). In the case of $NiSO_4 \cdot 6H_2O$ the nickel and sulphur atoms occupy the special positions with the symmetry of the two-fold axis of rotation. The six water molecules are said to be approximately octahedrally co-ordinated around the nickel ions. On the other hand, in $NiSO_4 \cdot 7H_2O$ the nickel and sulphur ions do not occupy any such symmetric special positions. Six of the seven water molecules are approximately octahedrally co-ordinated around the nickel ions in this case as well. In the case of $NiSO_4 \cdot 7H_2O$ as well as in $NiSO_4 \cdot 6H_2O$ there are four molecules per unit cell.

The degradation of the symmetry of the sulphate ion in the crystalline state and the consequent removal of the degeneracy of the oscillations results in the splitting of the degenerate oscillations, and hence all the nine frequencies of the SO_4 ion should appear. The coupling between the four molecules in the unit cell further increases the number of these internal oscillations. Thus, in the case of $NiSO_4 \cdot 7H_2O$ thirty-six components should appear whereas in the case of $NiSO_4 \cdot 6H_2O$ this number is only twenty-four owing to the higher symmetry of the crystal. Though the theoretically expected multiplicity of lines is not fully manifested in the spectra, the differences in the nature of the spectra due to the difference in the crystal symmetry and

tructure are evident. The breadth of some of the lines (*e.g.*, the group near 1100 cm.$^{-1}$) might be attributed to the overlapping of several of the components and their inadequate resolution.

The Raman spectrum of $NiSO_4 \cdot 7H_2O$ exhibits a close correspondence with the spectrum of $MgSO_4 \cdot 7H_2O$ (Shantakumari, 1953) the crystal structure of which is isomorphous with that of $NiSO_4 \cdot 7H_2O$. The following frequencies have been reported by her. 56, 75, 97, 118, 150, 252, 303, 445, 461, 609, 620, 986, 1059, 1064, 1076, 1098, 1134, 1148, 3185, 3228, 3338, 3406, 3446 and 3485 cm.$^{-1}$

Schaefer and Schubert (1916) report from their studies on the infra-red reflection spectrum of $NiSO_4 \cdot 6H_2O$, frequencies at 635, 1111, 1116, 2940, 3030 and 3125 cm.$^{-1}$ No infrared absorption studies appear to have been made with crystalline nickel sulphate.

In conclusion, the author wishes to express his sincere thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for the kind interest that he took during the course of this investigation.

5. SUMMARY

The Raman spectra of orthorhombic $NiSO_4 \cdot 7H_2O$ and the tetragonal $NiSO_4 \cdot 6H_2O$ have been investigated using the resonance radiation of mercury for excitation. Readily observable differences are exhibited by the spectra in the two cases which may be ascribed to the differences in crystal structure and symmetry.

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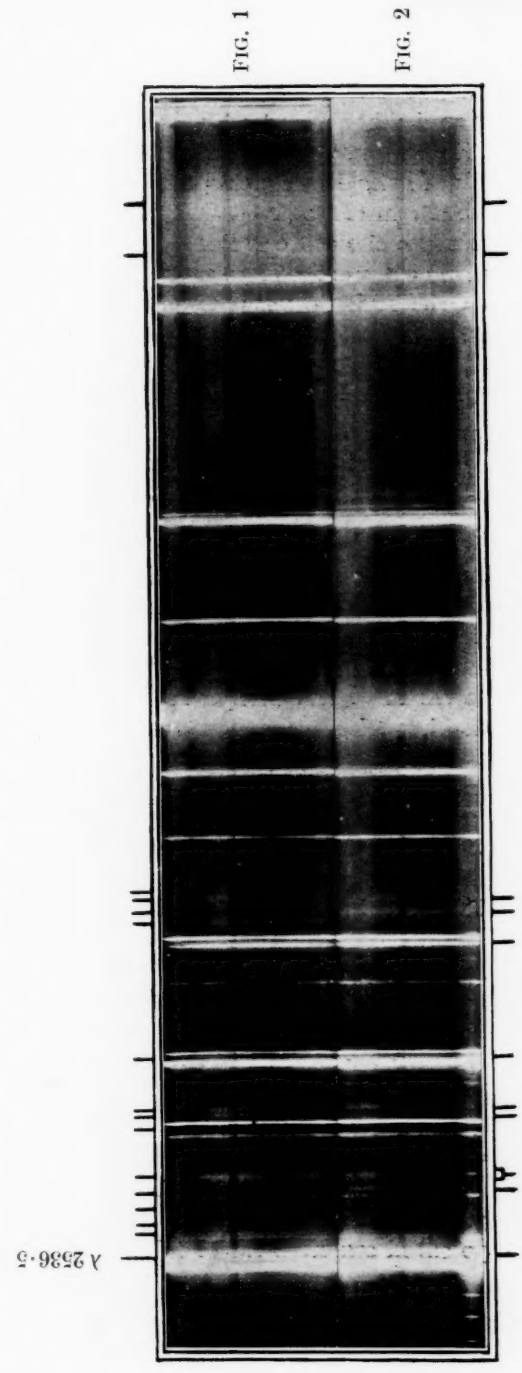

Raman Spectra of (1) $NiSO_4$. $7H_2O$ and (2) $NiSO_4$. $6H_2O$.

THE THERMAL EXPANSION OF CALCITE FROM ROOM TEMPERATURE UP TO 400° C.

By R. Srinivasan

(Department of Physics, Indian Institute of Science, Bangalore)

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1. Introduction

A study of the thermal expansion of calcite over a wide temperature range is of interest for the following reasons. Calcite belongs to the trigonal system and hence possesses two principal expansion coefficients—one along the optic axis and the other at right angles to it. Also its anisotropy of thermal expansion is large as it is the general case for crystals of the type $M(XO_3)$ (Lonappan, 1955). Its expansion coefficient perpendicular to the axis is negative and small. Such a negative expansion coefficient is of rare occurrence. Also its Raman and infrared spectra are known in great detail (1945, 1953). The temperature variation of its Raman spectrum has been investigated by Narayanaswamy (1946). Bhagavantam and Venkatarayudu (1939) have calculated the frequencies of all the normal modes of the crystal lattice employing a valence force field. Yet it is definitely not known whether calcite is typically ionic or typically of the valence type. X-ray studies indicate the former type; while its intense Raman spectrum is what is to be expected from a crystal belonging to the latter type. Chapman, Topping and Morral (1926) and Lennard Jones and Dent (1927) assumed a heteropolar force field and derived its lattice constant and other properties. An attempt at explaining the thermal expansion data in terms of the Raman and infrared spectra will be very interesting. The elastic constants of calcite have been measured by Bhimasenachar (1945). The specific heat, dielectric constant and a host of other physical properties have all been determined for calcite.

2. Previous Work

The thermal expansion of calcite has been measured near room temperature by Fizeau (1868) and Benoit (quoted in Weigle and Saini's paper) using the interference method. The expansion of calcite down to liquid hydrogen temperatures was measured by Adenstadt (1936) using the interference method.

The lattice expansion of calcite was measured by Megaw (1933) from room temperature to 100° C. She claims an accuracy of 10% and her

values are in good agreement with the macroscopic expansion values of Fizeau. Weigle and Saini (1934) determined the lattice constant and thermal expansion of calcite using its powder photograph taken with a Seeman-Bohlin camera. They used a crystal which was not very perfect as they felt that thermal expansion might not be affected by small impurities or lattice imperfections. They claim an accuracy of better than 1%. Yet their values for expansion between 0 to 100° C. are lower than those of Fizeau and Benoit. The discrepancy is large—about 20%. Yet they conclude that this should not be taken as evidence for any real difference between lattice and macroscopic expansion. Such a discrepancy might perhaps have been caused by the imperfections in the crystal. Recent experiments by Glover (1954) on the lattice expansion of pure and calcium-containing potassium chloride have definitely shown the influence of impurities to be negligible. In view of this finding, Weigle and Saini's data appear to be unexplainable.

No measurements of high temperature expansion are present and the present investigation was carried out to fill this lacuna.

3. Experimental Details

The experimental arrangement employed was that set up by Press (1949). The method of measurement has already been described in a previous paper by the author (1955). Preliminary measurements of the expansion coefficients both parallel and perpendicular to the axis were made by Mr. A. K. Sridhar; but he obtained anomalous results, probably because the orientations of his specimens were incorrect. The same specimens were used in the present investigations the orientation having been corrected with a polarising microscope. The specimens used finally were correct to within a degree of the required orientation. Three specimens were cut with the optic axis parallel to their bases. These were used to measure $\alpha_{\perp}$. Three others were cut with the optic axis perpendicular to their bases. These served to determine $\alpha_{\parallel}$.

4. Results and Discussion

The results of these measurements are given in Table I below. The curves showing the variation of $\alpha_{\parallel}$ and $\alpha_{\perp}$ with temperature are given in Fig. 1.

The pieces employed for determining $\alpha_{\perp}$ were only 0·312 cm. thick and as the expansion coefficient is very small, reliable measurements for the mean expansion coefficient over as much as 100° C. only could be obtained. Even then the accuracy of measurement is reduced and is about 5% in this case.

TABLE I

Values of $\alpha_{\parallel}$ and $\alpha_{\perp}$ for calcite at various temperatures

Range of Temp. ΔT° C.	Mean Temp. T° C.	$\alpha_{11}\times10^6$	Range of Temp. Δ T° C.	Mean Temp. T° C.	$\alpha_{\perp}\times10^6$
64–85	74·5	27·2	45–115	80	−5·78
85–105	94·9	28·2	70–150	100	−5·00
124–143	133·4	29·2	99–187	143	−4·57
179–198	188·9	29·9	143–241	192	−4·09
217–235	225·6	31·2	187–289	238	−4·09
250–268	259·3	31·4	241–347	294	−4·04
296–314	304·9	32·4	310–420	365	−3·83
330–348	338·5	33·0			
363–381	371·8	33·7			

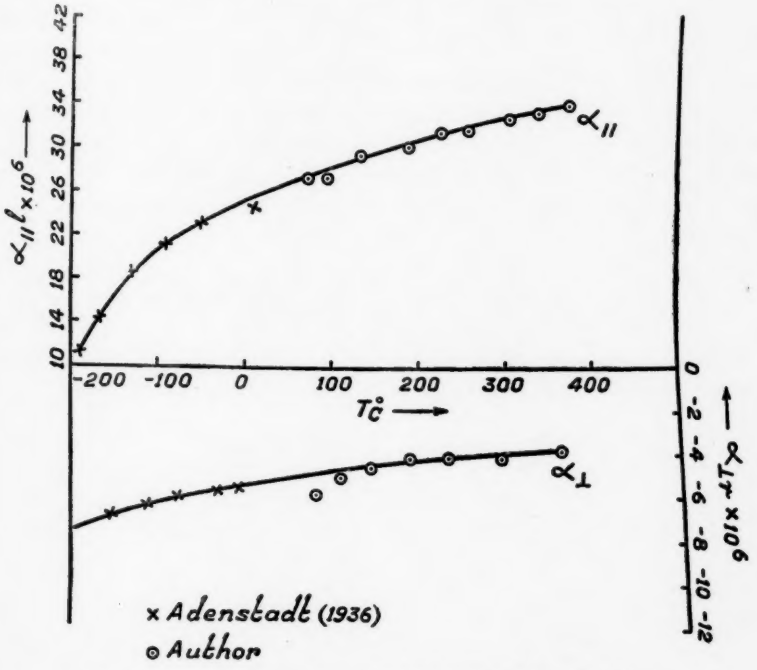

FIG. 1. Thermal Expansion of Calcite $\parallel^r$ and $\perp^r$ to the Axis.

The curves for $\alpha_{\parallel}$ and $\alpha_{\perp}$ as determined by the author are shown in Fig. 1. The low temperature expansion values of Adenstadt (1936) are plotted as crosses in the same figure. It is seen that the low temperature values of Adenstadt and the high temperature values of the author lie on a single curve for both $\alpha_{\parallel}$ and $\alpha_{\perp}$.

The values of $\alpha_{\parallel}$ and $\alpha_{\perp}$ as determined from the graph at 50° C. are compared with the values in literature.

$$\alpha_{\parallel} \text{ at } 50^{\circ}\text{ C.} = 26{\cdot}6\times10^{-6}$$

$$\alpha_{\perp} \text{ at } 50^{\circ}\text{ C.} = -\,5{\cdot}2\times10^{-6}$$

The values in the literature are

$\alpha_{\parallel} = 26{\cdot}2\times10^{-6}$ $\alpha_{\perp} = -\,5{\cdot}40\times10^{-6}$	Fizeau	$\alpha_{\parallel} = 25{\cdot}3 \pm 1{\cdot}5\times10^{-6}$ $\alpha_{\perp} = -\,5{\cdot}2 \pm 0{\cdot}7\times10^{-6}$	Megaw
$\alpha_{\parallel} = 25{\cdot}7\times10^{-6}$ $\alpha_{\perp} = -\,5{\cdot}50\times10^{-6}$	Benoit	$\alpha_{\parallel} = 21{\cdot}0\times10^{-6}$ $\alpha_{\perp} = -\,3{\cdot}8\times10^{-6}$	Weigle and Saini

The agreement with the values of Fizeau, Benoit and Megaw is very good. The values of Weigle and Saini are too low presumably because of the imperfect crystal they employed.

In the following table are collected the thermal expansion values $\alpha_{\parallel}$ and $\alpha_{\perp}$ at various temperatures, the volume expansion coefficient β, the specific heat per gram c_p and the Gruneisen constant γ. The values of c_p have been taken from *International Critical Tables*; the value of the compressibility χ is taken as $15{\cdot}4\times10^{-13}$ sq.cm./dyne from Bhimasenachar (1945).

TABLE II

The linear expansion coefficients $\alpha_{\parallel}$ and $\alpha_{\perp}$, the volume expansion coefficient β, the specific heat and the Gruneisen constants for calcite at different temperatures

Compressibility $\chi = 1{\cdot}54\times10^{-12}$. Molar Volume V = 34·2 c.c.

T° C.	$\alpha_{11}\times10^{6}$	$\alpha_{\perp}\times10^{6}$	$\beta\times10^{6}$	c_p joules/gm.	Gruneisen Const. γ
−150	16·4	−6·8	2·8	0·452	0·14
−100	20·6	−6·3	8·0	0·590	0·30
0	25·0	−5·4	14·2	0·763	0·41
100	28·1	−4·9	18·3	0·870	0·47
200	30·8	−4·2	22·4	0·962	0·52
300	32·8	−3·9	25·0	1·046	0·53

As usual the Gruneisen constant decreases with decreasing temperatures. The small value of the Grunesien constant is noteworthy as it is typical for a valence crystal. The intense Raman spectrum of calcite and its dielectric polarisation also point to such a type of binding in the crystal.

The author is indebted to Prof. R. S. Krishnan who suggested this problem and provided the specimens. He is also thankful to Dr. Vedam for his help in determining the orientation of the specimens.

5. Summary

The thermal expansion of calcite along and perpendicular to the optic axis were measured from room temperature up to 400° C. $\alpha_{\parallel}$ increased with increasing temperature, while $\alpha_{\perp}$, which is negative, decreases in magnitude with increasing temperatures. The high temperature curves join up well with the low temperature curves of Adenstadt. The Gruneisen constant is shown to vary with temperature in the usual manner. Its small value points to a valence type of binding in the crystal—a fact supported by the intense Raman effect and dielectric polarisability of calcite.

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THE PROPAGATION OF LIGHT IN ABSORBING BIAXIAL CRYSTALS—I. THEORETICAL

By S. Pancharatnam

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1. Introduction

Absorbing biaxial crystals in general display a variety of remarkable optical phenomena in the vicinity of both the optic axes. For example, if an extended source of unpolarised light is viewed through a plate of highly pleochroic material cut normal to an optic axis, two dark brushes—the Brewster's brushes—are generally seen in the field of view; while if a polariser be inserted in front of the plate, the so-called idiophanic rings are observed—similar to the interference rings that can appear in the case of a transparent crystal *if an analyser be also present.*

The theoretical investigations of Waldemar Voigt focussed attention on the fact that certain of the features relating to the propagation of light in the vicinity of an optic axis differ radically from those obtaining in transparent media. Thus, whereas along any general direction in a transparent crystal there are two particular linearly polarised vibrations that can be propagated without change of form, this is no longer the case in absorbing crystals. As a matter of fact, close to an optic axis and on either side of it, there even exist two directions—the singular axes—with the following remarkable properties: *only* a right-circular vibration can be propagated without change of form along one of these axes, and *only* a left-circular vibration along the other.* In this paper it will be shown that the various features of the propagation of light in absorbing media may also be conveniently regarded as due to the superposed effects of birefringence and dichroism. Because of the simplicity of the method, it has also been possible to make a more detailed investigation of the following interesting question: what will happen when, for example, a right-circular vibration is incident in the direction of a singular axis where only a left-circular vibration can be propagated without change of form? The results obtained in this connection are at variance with those expected by Voigt (Section 6).

* A non-mathematical summary, in English, of the main results of Voigt's investigations may be found in Reference 1.

The analysis of the propagation of light in absorbing biaxial media from the standpoint of the electromagnetic theory has been discussed by several authors. The comparatively simple case of orthorhombic crystals (where the principal axes of the dielectric tensor and the complex conductivity tensor necessarily coincide) is discussed in Drude's treatise.[2] But the somewhat oversimplified presentation there given omits entirely those theoretical and experimental features with which we shall be particularly concerned. These may be found described in more detailed treatments,[3-5] particularly those of Voigt and Pockels. In view of the complexity of the phenomena involved, it would appear that a consideration of the problem from a simpler though less rigorous standpoint would certainly be useful. Such an approach is provided in the present paper, and, as we shall show, the method adopted leads to results that are practically identical with those of the electromagnetic theory.

2. General Features of Light Propagation in Absorbing Media

(*a*) *The Index and Absorption Ellipsoids*

In an absorbing biaxial medium not possessing optical activity, the two waves propagated along any direction appreciably inclined to both the optic axes may be regarded as practically plane polarised (though not rigorously so, as in the transparent crystal). And as in a transparent crystal their 'vibration-directions' may then be considered to lie on the principal planes, their velocities being determined by their vibration-directions thus: the reciprocal of any radius of a so-called *index ellipsoid* gives the velocity for vibrations parallel to that radius. In addition, the two waves have different coefficients of extinction κ_1 and κ_2, these being determined again by their vibration-directions thus: the reciprocal of any radius of a so-called *absorption ellipsoid* gives the value of $\sqrt{(2\kappa v^3/c)}$ for vibrations parallel to that radius, v being the velocity for that vibration-direction.

By assuming that the above statements hold good even for directions in the vicinity of an optic axis, it is indeed possible to explain *some* of the phenomena observed there—and such a procedure is in fact followed in Drude's treatise. For example, the occurrence of Brewster's brushes can be explained along the following lines. In the neighbourhood of an optic axis, a comparatively small change in the direction of propagation will in general cause an appreciable change in the inclinations of the two principal planes to the axial plane; this in turn will lead to a large variation in the total absorption, since the absorption coefficients of the two waves will be determined by the orientation of their vibration-directions.

(*b*) *The Elliptical Polarisation of the Waves*

The appearance of idiophanic interference rings with a polarizer *alone* cannot however be explained on the assumption that the light incident along any direction is split up into two linearly polarized beams with their vibrations at right angles to one another; their states of polarization being *orthogonal*, two such beams will be incapable of interference with one another (unless brought to the same plane of vibration by an analyser).

The fact is that when we turn to directions of propagation in the vicinity of an optic axis, we are no longer justified in neglecting a remarkable and important consequence of the phenomenological theory: namely, that the two waves propagated in any general direction in an absorbing biaxial medium are in reality, *elliptically polarized.* Though the two elliptic vibrations have their axes *majores* at right angles, and their ellipticities equal, they are rendered *non-orthogonal* by the fact that they are of the *same* handedness; and this last mentioned feature (together with the fact that the major axes do not in general coincide with the principal planes) distinguishes the situation sharply from that obtaining in optically active (transparent) crystals.

In the context of the elliptical polarisation of the waves, the index and absorption ellipsoids—strictly speaking—retain significance only in terms of the dielectric and conductivity-like tensors by means of which they are *defined.* Nevertheless, as we shall show, the existence of the two non-orthogonal elliptically polarised waves may be conveniently treated as due to the superposed effects of birefringence and dichroism—just as the propagation of two orthogonal elliptically polarised waves near to an optic axis in an optically active transparent medium, may (by Gouy's hypothesis[4,6]) be conveniently treated as due to the superposed effects of birefringence and rotation.

3. THE SUPERPOSITION OF BIREFRINGENCE AND DICHROISM

Consider a plate cut perpendicular to an arbitrary direction z which is also taken as being normal to the plane of the paper. Let OX_r and OY_r (Fig. 1) be the trace of the principal planes of refraction—defined as usual, either in terms of the index ellipsoid or the optic binormals. Similarly let OX_k and OY_k be the trace of the *principal planes of absorption*—which we shall define analogously, *either* as containing the major and minor diameters of the elliptical section of the absorption ellipsoid made by the plane of the paper, *or* as the internal and external bisectors of the angle subtended on the z-direction by the two absorption-binormals (normals to the circular sections of the absorption ellipsoid).

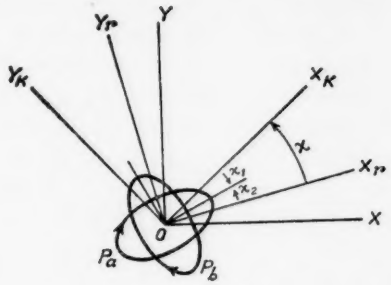

FIG. 1

P_a and P_b—States of polarisation propagated unchanged.
OX_k and OY_k—Trace of the principal planes of absorption.
OX_r and OY_r—Trace of the principal planes of refraction.

Consider an arbitrary elliptic vibration P (which, for the sake of concreteness, may be temporarily identified with the one marked P_a in the figure). In the absence of absorption the arbitrary elliptic vibration P will be resolved into two vibrations (along the principal planes of refraction, OX_r and OY_r) between which an infinitesimal phase difference δdz will be introduced corresponding to a passage dz. Since, however, anisotropic absorption is also present, we perform, in addition, the infinitesimal operation of linear dichroism; the elliptic vibration—as modified by the infinitesimal operation of birefringence—is resolved into two linear vibrations (this time, along the principal planes of absorption, OX_k and OY_k), the amplitudes of which are then reduced by the multiplying factors $(1 - k_1 dz)$ and $(1 - k_2 dz)$ respectively. The differential absorption of the two components will cause the state of the elliptic vibration to ' move towards ' the state of polarisation of the less absorbed component OX_k (a phrase which acquires a more vivid meaning in the Poincaré sphere representation). Those states of polarisation alone can be propagated without change of form, which under the successive infinitesimal operations of birefringence and dichroism (applied in either order) remain unaltered in form and orientation—and to these states of polarisation alone can definite velocities of propagation and coefficients of absorption be assigned.

Several particular cases may first be noted. Along the optic axial directions where the birefringence vanishes, the two waves (propagated with different coefficients of absorption) are linearly polarised along the principal planes of absorption. Similarly, the waves propagated along directions appreciably inclined to the optic axes will be practically plane polarised along

the principal planes of refraction, since the absolute values of the dichroism (k_2-k_1) is usually such that it is very small compared with the birefringence $(\delta_1-\delta_2)$ along such directions. Also, where the principal planes of absorption and refraction coincide (as for example along the axial plane in orthorhombic crystals) the waves will be rigorously linearly polarised along the common principal planes.

The more general case, where the solution is not so apparent, is discussed analytically in Section 7, but the main results will first be proved more briefly and elegantly by the use of the Poincaré sphere. For this purpose, the form of the arbitrary elliptic vibration P—as distinct from its intensity and absolute phase—must first be specified by means of certain parameters. The principal planes of absorption and refraction form the two natural co-ordinate systems to which the vibration P may be referred. The ratio $\tan\phi$ of the amplitudes of the components of the vibration P along OY_r and OX_r does not by itself completely specify the form of the elliptic vibration (since the phase difference θ_r between these components has also to be given). Similarly the ratio $\tan\psi$ of the amplitudes of the components of P along OY_k and OX_k does not by itself completely specify the form of P (since the phase difference θ_k between these components has also to be given). But ϕ and ψ together form two convenient symmetrical parameters completely specifying the form of the elliptic vibration $P(\phi, \psi)$—provided we separately give the sense of description of the ellipse. It may also be noted that apart from an intensity factor, $\cos 2\phi$ and $\cos 2\psi$ are the two values of the second Stokes parameter M of the vibration $P(\phi, \psi)$ when it is referred successively to co-ordinate systems along the principal planes of refraction and absorption respectively.

As indicated in the figure, it turns out that there are two particular elliptic vibrations described in the same sense, $P_a(\phi_a, \psi_a)$ and $P_b(\phi_b, \psi_b)$, that can be propagated without change of form under the superposed effects of birefringence and dichroism. The form of the vibration P_b can be obtained from that of P_a merely by rotating the latter by 90° in its own plane—which means that ϕ_b and ψ_b are complementary to ϕ_a and ψ_a respectively.

4. USE OF THE POINCARÉ SPHERE FOR SUPERPOSITION

(*a*) *The General Method*

The Poincaré sphere,[4,7] which has proved very useful for the analysis of the propagation of polarised light in *transparent* media, turns out also to be of great use in our present discussion on absorbing crystals.

As is well known, a one-to-one correspondence can be set up between all the points on the surface of a sphere (the Poincaré sphere) and all the possible forms of elliptic vibrations that can be conceived (circular and linear vibrations being regarded as particular cases of elliptic vibrations). In particular the arbitrary elliptic vibration P referred to in the previous section is represented by a corresponding point P on the Poincaré sphere, while a linear vibration along OX_k will be represented by some other point X_k. The infinitesimal operation of anisotropic absorption described in the last section will obviously alter the form of the elliptic vibration P in such a manner that one may say it gets more polarised in the direction of OX_k, since this is the less absorbed component. This infinitesimal alteration in the state of the elliptic vibration P corresponds (on the Poincaré sphere) to an infinitesimal movement of the point P directly towards X_k, *i.e.*, along the direction of the shortest arc joining them.

Similarly the infinitesimal alteration in the state of the (initial) elliptic vibration P due to the operation of birefringence alone, corresponds to an infinitesimal movement ds_r of the representative point P. If the elliptic vibration is to be propagated without change of form, this movement ds_r should be equal and opposite to the displacement of P due to dichroism alone; and the problem of finding the states of polarisation that can be propagated without change of form is therefore reduced to the simple geometrical problem of finding the points P on the Poincaré sphere which satisfy the above requirement.

(*b*) *The Operations of Dichroism and Birefringence*

Referring to Fig. 2, let X_k and Y_k give the orientations of the principal planes of absorption. (The arbitrary elliptic vibration P has not been indicated on the sphere, but for the sake of concreteness, may be temporarily identified with the particular state P_a in the figure.) If the elliptic vibration P is resolved into two orthogonal linear vibrations in the states X_k and Y_k, then the amplitudes F_k and G_k of these components will be proportional to $\cos\psi$ and $\sin\psi$, where 2ψ is the angular distance of the point P from X_k on the Poincaré sphere. (For a proof of this statement, see reference 7.) Hence $G_k/F_k = \tan\psi$. If the amplitudes of these components are reduced by the multiplying factors $e^{-k_1 z}$ and $e^{-k_2 z}$, the angular distance of P from X_k will change from 2ψ to $2\psi'$ where:

$$\tan\psi' = \frac{G_k\, e^{-k_2 z}}{F_k\, e^{-k_1 z}} = \tan\psi\, e^{-(k_2-k_1)\, z} \qquad (1)$$

Since the phases of the X_k and Y_k components of P are to be left unaltered in this operation, the movement of P will be entirely on the meridional arc

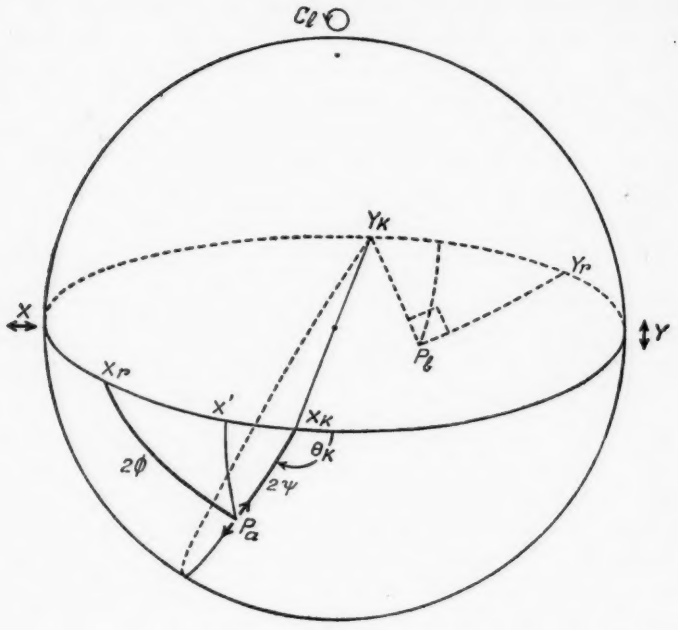

FIG. 2

(X_k, Y_k) and (X_r, Y_r)—Principal planes of absorption and refraction, respectively.
P_a and P_b —States of polarisation propagated unchanged.
$X_rX_k = 2\chi$; $X_kX' = 2\chi_1$; $X_rX' = 2\chi_2$; $P_aX' = 2\theta$.

Y_kPX_k. This follows from the fact that *the X_k and Y_k components of all elliptic vibrations on this arc have the same phase difference* θ_k (where θ_k is the angle indicated in Fig. 2); for, if an additional phase difference $-\theta_k$ be introduced between these components, any such elliptic vibration will be reduced to a linear vibration on the equatorial arc $X_kY_rY_k$ (by a well known property of the Poincaré sphere).

The infinitesimal operation of linear dichroism (corresponding to a passage dz) will, apart from reducing the intensity, cause the initial state of polarisation P to move along the arc PX_k towards the state X_k (the less absorbed component), through an arc $ds_k = -2d\psi$. From (1) we have

$$\tan\psi + d(\tan\psi) = [1 - (k_2 - k_1)\,dz]\tan\psi$$

or

$$2\sec^2\psi d\psi = -2(k_2 - k_1)\,dz.\tan\psi$$

which leads to the simple relation

$$ds_k = (k \sin 2\psi)\, dz \tag{2}$$

where

k denotes $(k_2 - k_1)$

Let X_r and Y_r represent the orientations of the principal planes of refraction, the former corresponding to the slower wave in the absence of absorption; let δ denote the phase difference $(\delta_1 - \delta_2)$ introduced per unit distance (in the absence of dichroism). The infinitesimal operation of birefringence (corresponding to a passage dz) consists in rotating the sphere clockwise about the equatorial diameter $X_r\, Y_r$ through the infinitesimal angle δdz. This operation will cause the initial state of polarization P to move along the arc of a small circle with X_r as pole through an arc ds_r, where

$$ds_r = (\delta \sin 2\phi)\, dz \tag{3}$$

(*c*) *The States of Polarisation Propagated Unchanged*

In order that the simultaneous superposition of linear dichroism and birefringence should cause no change in the state of P, the movements ds_k and ds_r must be equal in magnitude and opposite in direction. Since arc ds_k is along PX_k while arc ds_r is perpendicular to PX_r we must have firstly, $X_r PX_k = \pi/2$, or

$$\cos 2\chi = \cos 2\phi \cos 2\psi \tag{4}$$

and secondly

$$\delta \sin 2\phi = k \sin 2\psi \tag{5}$$

together with the condition that P will be a right- or left-elliptic vibration according as χ (the angle between the X_k and X_r axes) is positive (0 to $\pi/2$) or negative (0 to $-\pi/2$).

In general there are two positions P which simultaneously satisfy these conditions—the relations (4) and (5) being unchanged when we alter 2ϕ and 2ψ to $\pi - 2\phi$ and $\pi - 2\psi$ respectively. Thus in the figure the state P_b whose distances from the points Y_k and Y_r are 2ψ and 2ϕ, is also propagated unchanged. The states P_a and P_b have the same latitudes, their longitudes differing by π.

Hence we arrive at the result, also obtained from the electromagnetic theory, that the states of polarisation propagated unchanged along any general direction are two similarly rotating elliptic vibrations which have their major axes crossed and their ellipticities equal.

In order to construct these two elliptic vibrations (see Fig. 1) we must first determine the orientations of one of the principal diameters—for example the orientation of OX′ which is the major axis of P_a and also the minor axis of P_b. Let the inclination of OX′ be χ_2 (anti-clockwise) with respect to OX_r and χ_1 (clockwise) with respect to OX_k. The direction of OX′ may be determined by the relation

$$\frac{\sin 4\chi_1}{\sin 4\chi_2} = \frac{\delta^2}{k^2} \tag{6}$$

Next the ratio $\tan\theta$ of the minor to the major axis of the elliptic vibrations may be obtained from

$$\sin^2 2\theta = \tan 2\chi_1 \tan 2\chi_2 \tag{7}$$

—a relation which gives the ellipticity ($\tan\theta = \operatorname{cosec} 2\theta + \sqrt{\operatorname{cosec}^2 2\theta - 1}$) in terms of the orientation of the axes of the elliptic vibrations. It may be noted that equations (6) and (7) remain unaltered when we change χ_1 and χ_2 to $(\pi/2 + \chi_1)$ and $(\pi/2 + \chi_2)$ respectively.

The relations stated in the previous paragraph will now be proved with the aid of the Poincaré sphere (Fig. 2). The direction OX′ is given by the point X′ on the equator having the same longitude as P. Then since the triangles X_rPX' and X_kPX' are both right-angled, we have

$$\left.\begin{aligned} \cos 2\phi &= \cos 2\chi_2 \cos 2\theta \\ \cos 2\psi &= \cos 2\chi_1 \cos 2\theta \end{aligned}\right\} \tag{8}$$

Multiplying these equations and comparing with (4),

$$\cos(2\chi_1 + 2\chi_2) = \cos 2\chi_1 \cos 2\chi_2 \cos^2 2\theta$$

which on simplification gives the relation (7).

To prove (6) we consider the right-angled triangles X_kPX_r and X_kPX':

$$\cos \hat{X}_k = \frac{\tan 2\psi}{\tan 2\chi} = \frac{\tan 2\chi_1}{\tan 2\psi}$$

Hence

$$\tan^2 2\psi = \tan 2\chi_1 \tan 2\chi$$

$$\tan^2 2\phi = \tan 2\chi_2 \tan 2\chi$$

or,

$$\frac{\tan^2 2\psi}{\tan^2 2\phi} = \frac{\tan 2\chi_1}{\tan 2\chi_2} \tag{9}$$

From relations (8) we also have

$$\frac{\cos^2 2\psi}{\cos^2 2\phi} = \frac{\cos^2 2\chi_1}{\cos^2 2\chi_2} \tag{10}$$

Multiplying (9) and (10) and comparing with (5) we get the required relation (6).

(*d*) *Comparison with the Electromagnetic Theory*

The relation (7) giving the ellipticity in terms of the orientation of the axes of the elliptic vibration, is identical with that deduced from the electromagnetic theory (Pockels, *loc. cit.*, p. 399, eq. 54); while the relation (6) giving the orientation of the axes of the elliptic vibrations has to be compared with the following similar relation (Pockels, *loc. cit.*, p. 397, eq. 53):

$$\frac{\sin 4\chi_1}{\sin 4\chi_2} = \frac{\rho^2}{\sigma^2} \tag{6'}$$

where

$$\rho = \tfrac{1}{2}(a_2 - a_1) \text{ and } \sigma = \tfrac{1}{2}(b_2 - b_1)$$

The tensor components a_1, a_2, etc., may be easily shown to have the following geometrical meanings. The major and minor semi-axes of the elliptical section of the index ellipsoid made by the plane of the paper have lengths $1/\sqrt{a_1}$ and $1/\sqrt{a_2}$ respectively, while the major and minor semi-axes of the elliptical section of the absorption ellipsoid have lengths $1/\sqrt{b_1}$ and $1/\sqrt{b_2}$ respectively. Relations (6) and (6′) will be identical if

$$\delta^2/k^2 = \rho^2/\sigma^2 \tag{11}$$

As pointed out in Section 2, the waves propagated along directions appreciably inclined to the optic axes may be considered as linearly polarised; and for such directions of propagation, if $1/\sqrt{b}$ be the length of any radius of the absorption ellipsoid, then $b = 2\kappa v^3/c$, where κ is the extinction coefficient and v the velocity for that vibration-direction. In consonance with this it would be natural to use the following relation for the hypothetical extinction coefficients κ_1 and κ_2 in the absence of birefringence:

$$\frac{2\kappa_1 v_m^3}{c} = b_1 \; ; \; \frac{2\kappa_2 v_m^3}{c} = b_2 \tag{12}$$

where v_m is a mean velocity. We then have

$$k = \frac{2\pi}{\lambda_0}(\kappa_2 - \kappa_1) = \frac{2\pi c}{\lambda_0}\frac{\sigma}{v_m^3}$$

Relation (11) will be obviously satisfied if we analogously set

$$\delta = \frac{2\pi c}{\lambda_0} \cdot \frac{\rho}{{v_m}^3} = \frac{2\pi c}{\lambda_0} \cdot \frac{a_2 - a_1}{2{v_m}^3} \tag{13}$$

Since the velocoties v_1 and v_2 in the absence of absorption are equal to $\sqrt{a_1}$ and $\sqrt{a_2}$ respectively, relation (13) will be *exactly* satisfied if we define the mean velocity v_m by

$${v_m}^3 = \tfrac{1}{2}(v_1 + v_2) \cdot v_1 v_2 \tag{14}$$

5. The Absorption Coefficients and Refractive Indices of the Waves

It is well known that in the case of a transparent crystal, it is simpler to specify the velocities of the waves as functions of the vibration directions than as functions of the directions of propagation: the former leads to the simple index-ellipsoid representation, the latter to the comparatively more complex wave surface of two sheets. We shall show that for absorbing crystals too, if we choose to express the velocities and absorption coefficients as functions of the states of polarisation (ϕ, ψ) of the waves, the resulting expressions (as deduced both by the method of superposition and by the electromagnetic theory) may be put in a very simple form.

When an elliptic vibration of unit intensity in any state of polarisation travels a distance dz, the diminution in its intensity may be calculated directly from the reduction of intensity involved in the infinitesimal operation of dichroism corresponding to the passage dz—since the operation of birefringence produces no reduction in intensity. If, in addition, the elliptic vibration be in a state of polarisation P_a that can be propagated without change of form, this reduction in intensity may be equated to $2k_a\,dz$ where k_a is the coefficient of absorption for that wave. The amplitudes of the X_k and Y_k components of the elliptic vibration P_a will be $\cos\psi_a$ and $\sin\psi_a$ respectively; hence the reduction in intensity of these components will obviously be $2k_1\cos^2\psi_a\,dz$ and $2k_2\sin^2\psi_a\,dz$ respectively. Therefore,

$$\left.\begin{aligned} k_a &= k_1\cos^2\psi_a + k_2\sin^2\psi_a \\ \text{Similarly}\quad k_b &= k_1\sin^2\psi_a + k_2\cos^2\psi_a \\ \text{So that}\quad (k_a - k_b) &= (k_1 - k_2)\cos 2\psi_a \end{aligned}\right\} \tag{15}$$

Here 2ψ being the arc PX_k on the Poincare sphere may be evaluated by the relations (4) and (5) of Section 4*c*, which determine the states of polarisation of the waves.

Expressions for the refractive indices of the waves (in terms of the state of polarisation of one of them) are equally simple, being given by:

$$\left.\begin{aligned} n_a &= n_1 \cos^2 \phi_a + n_2 \sin^2 \phi_a \\ n_b &= n_1 \sin^2 \phi_a + n_2 \cos^2 \phi_a \\ (n_a - n_b) &= (n_1 - n_2) \cos 2\phi_a \end{aligned}\right\} \qquad (16)$$

The proofs of these relations do not have the same simplicity as those of (15), and will be given only at the end of Section 7, since recourse must be taken to the analytically derived equations obtained there.

(6) The Propagation of Light along the Axes of Circular Polarisation

(*a*) *The Singular Axes*

The electromagnetic theory predicts that close to an optic axis and on either side of it, there exist two directions along each of which only *one* state of polarisation (and not two) can be propagated unchanged: only a right-circularly polarised wave can be propagated along one of these axes, and only a left-circularly polarised wave along the other. These directions have been termed the *Windungsachsen*; Voigt has also referred to them as *singular axes* and we shall follow this simpler nomenclature. At these two axes of circular polarisation the inclinations of the principal planes of absorption with respect to the *corresponding* principal planes of refraction are $+45°$ and $-45°$ respectively. Further, along these two directions the pure birefringence term δ is equal to the dichroic term k.

The remarkable property of these axes follows very simply from the standpoint of the method of superposition by the use of the Poincaré sphere. Let us suppose for example that the principal plane of absorption OX_k makes an angle of $-45°$ with respect to the corresponding principal plane of refraction OX_r. In Fig. 3, the diameter X_kY_k will then be at right angles to X_rY_r as shown. If we consider a state of polarisation initially coincident with the pole C_l, it can be seen that its movement ds_r (due to an infinitesimal clockwise rotation δdz, about X_rY_r) will be oppositely directed to the movement ds_k towards the less absorbed component X_k; and the movements will be equal in magnitude if $\delta = k$. Thus a left-circular vibration can be propagated unchanged along such a direction. Further, there can be no other state which can also be propagated unchanged, since the 2 elliptic vibrations propagated unchanged along any direction must have the same sense of description and the same ellipticity. Similarly, where OX_k makes an angle

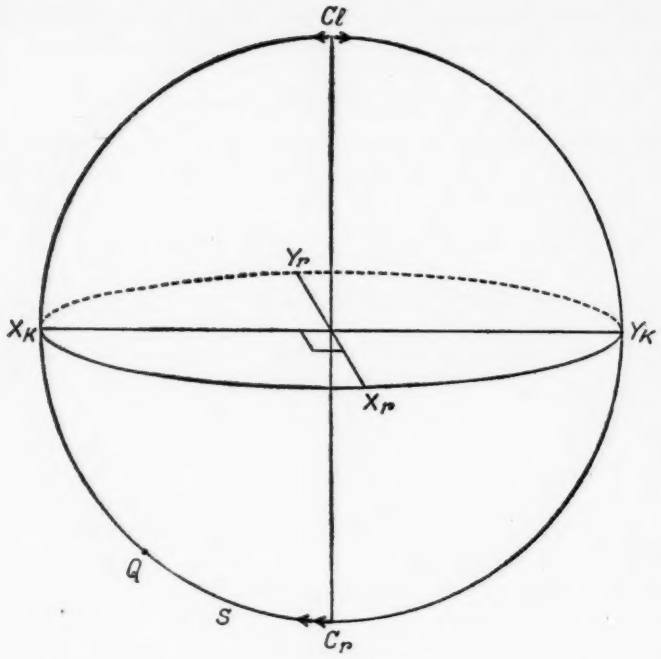

FIG. 3

C_r—Right circular vibration incident in the direction of a singular axis (where only the left-circular vibration C_l can be propagated unchanged).

Q—The state of vibration at a depth z (specified by the arc s).

of $+45°$ with respect to OX_r, and where in addition $\delta = k$, only a right-circular vibration can be propagated unchanged. The refractive index of the circularly polarised wave that can be propagated unchanged along a singular axis is $\frac{1}{2}(n_1 + n_2)$ and its absorption coefficient $\frac{1}{2}(k_1 + k_2)$ as may be seen by setting $\phi = \psi = \pi/4$ in relation (18) and (19).

Before proceeding to discuss in more detail the propagation of light along the singular axes, we consider it relevant to point out that the functions with which we are concerned show no discontinuity at the singular axes. Thus both the elliptic vibrations propagated without change of form along any general direction, gradually degenerate into two (identical) circular vibrations as we approach a singular axis from any side whatsoever. [This can be seen by making $\chi \to 45$ and $\delta \to k$ in relations (4) and (5) of Section 4 *c*.] The refractive indices and absorption coefficients of these two waves, being determined by their states of polarisation (by relations 15 and

16 of Section 5) tend towards the common values $\frac{1}{2}(n_1 + n_2)$ and $\frac{1}{2}(k_1 + k_2)$ respectively, as we approach a singular axis. (See also reference 8.)

(*b*) *Effects with Incident Circularly Polarised Light*

In this section we shall inquire as to what will happen when, for example right circularly polarised light C_r is incident in the direction of a singular axis where only a left circular vibration C_l can be propagated unchanged (Fig. 3). Our results in this connection are at variance with those expected by Voigt. It was supposed by Voigt[3, 4] that if a plate cut normal to an optic axis is viewed in convergent circularly polarised light, then along the singular axis where the incident vibration can be propagated unchanged, more light would get through than in the neighbourhood of the other singular axis where only the oppositely directed circular vibration can be propagated unchanged; and that the latter direction should in consequence appear darker than the former.* On performing an actual experiment, he observed a dark and a bright spot in the field of view, one on either side of the optic axis and this was considered by him as confirming his view. According to our analysis, however, it is the singular axis where the incident vibration can be propagated unchanged that should appear *darker* than the other singular axis (where only the oppositely directed circular vibration can be propagated *unchanged*).

We shall apply *directly* the method of superposition, according to which, given the state of vibration at a particular plane in the medium, the state of the vibration at a further distance *dz* is obtained by superposing the effects of pure birefringence and pure dichroism corresponding to that passage. The state of vibration should then get progressively altered as we proceed into the medium.

Referring to Fig. 3, if the state of polarisation be initially coincident with the pole C_r, its movement ds_r (due to a clockwise rotation δdz about X_rY_r) is in the *same* direction as its movement ds_k towards the less absorbed component X_k; and the sum of these movements will give the alteration in the state of vibration corresponding to a passage *dz*. Continuing this procedure, it can be seen that as we proceed into the medium, the state of polarisation progressively moves along the arc $C_rX_kC_l$. At a particular depth the vibration would be linearly polarised along the principal plane

* In a later paper [8], Voigt has suggested that if we could get a plate exactly normal to a singular axis, and have circularly polarised light of the proper sense incident precisely along this normal, the light would be *totally* reflected—the reflection being partial in practical cases. This idea receives no support from the results of the present investigation.

of absorption OX_k. After this stage the movement ds_k due to dichroism opposes the movement ds_r due to birefringence; but the latter being greater in magnitude, the state of polarisation continues to alter as we proceed further into the medium, tending towards the state C_l that can be propagated without change of form.

Thus if we consider the state of polarisation at successive depths within the medium, we see that the incident right-circular vibration will first get modified to an elliptic vibration (with major axis always at 45° to the principal planes of refraction), which in turn gets reduced to a linear vibration; as we proceed further the linear vibration opens out into a *left-handed* elliptic vibration, which gradually tends towards the state of a left-circular vibration that can be propagated unchanged. Nevertheless, as may be seen physically, this last state is never attained at any finite depth; for as the state of polarisation comes close to that of a left-circular vibration, the modification of the state corresponding to an additional passage dz becomes correspondingly reduced.

It is easy to deduce an explicit expression for the state of polarisation P that should be expected (according to the above line of argument) at any depth z inside the medium. The state P may be specified by giving the length s of the arc C_rP. Then the state $s + ds$ at the depth $z + dz$ will be given by

$$ds = (\delta + k \cos s)\, dz \tag{17}$$

according to relations (2) and (3) of Section 4 *b*. Since $\delta = k$, we have on integration,

$$\tan \tfrac{1}{2}s = kz \tag{18}$$

This relation shows that the transformation from a right-circular vibration ($s = 0$), to a linear vibration at 45° to the principal planes of refraction ($s = \pi/2$), occurs within a smaller depth than if the crystal had been transparent; whereas the corresponding alteration from the linear vibration to a left circular vibration (which for a transparent crystal would have occurred at a finite depth) requires here an infinite passage, due to the 'retarding' effect of the dichroism.

We shall next calculate the intensity I_z of the vibration P at a distance z inside the medium. The diminution of intensity $-dI_z$ corresponding to an additional passage dz is given by

$$-dI_z/I_z = 2k_z dz \tag{19}$$

where, it must be noted k_z is not a constant but a function of the state of polarisation and hence also of the depth z. We will have for k_z an expression

analogous to (15), Section 5:

$$k_z = k_1 \cos^2 \psi + k_2 \sin^2 \psi$$
$$= \tfrac{1}{2}(k_1 + k_2) - \tfrac{1}{2}k \cos 2\psi \qquad (20)$$

Thus k_z is always less than the coefficient of absorption $\frac{1}{2}(k_1 + k_2)$ of the left-circularly polarised wave that can be propagated without change of form along the same direction. (This is more directly seen by the fact that the state of polarisation is always nearer to the less absorbed component X_k than is a left-circular vibration.) Hence *when the sense of description of a circular vibration incident in the direction of a singular axis is* opposed *to that which can be propagated unchanged along that direction, the emergent intensity should in fact be* greater *than when the sense of description of the incident vibration is reversed.* An expression for the ratio of the emergent intensities in the two cases will now be deduced. Since, from our point of view, the incident disturbance can propagate into the medium in both cases (though in one case with a progressive change in the state of polarisation) we have no particular reason to assume that the reflection losses would be different in the two cases.

Substituting the value of k_z given by (20) in (19) we get

$$-dI_z/I_z = (k_1 + k_2)\,dz - k \sin s\,dz$$

Expressing sin s in terms of z by using relation (18), and integrating, we have —if I_1 be the emergent intensity and I_0 the intensity entering the medium,

$$\log (I_0/I_1) = (k_1 + k_2)\,z - \log (1 + k^2 z^2) \qquad (21)$$

On the other hand if I_2 be the emergent intensity when the incident circular vibration is of the sense which can be propagated unchanged,

$$\log (I_0/I_2) = (k_1 + k_2)\,z \qquad (22)$$

From (21) and (22) we have the following simple relation for the ratio of the intensities emerging in the two cases:

$$I_1/I_2 = 1 + k^2 z^2$$

a ratio which is always greater than unity.

Though our results regarding the properties of the singular axes are at variance with those expected by Voigt, it must not therefore be concluded that the method of superposition leads to results differing from the electromagnetic theory—since it is possible to regard the former merely as a mathe-

matical artifice: for (as has been pointed out in Section 8), by reversing the entire scheme of arguments, the propagation of two elliptically polarised waves with different absorption coefficients and velocities (*as given by the electromagnetic theory*) may for mathematical convenience be rigorously treated by the method of superposition; the convenience of this artifice being particularly manifest when we wish to find the limiting effects as the two elliptically polarised waves gradually tend towards the state of two (identical) circularly polarised waves with equal velocities and absorption coefficients.

7. Analytical Discussion of Superposition

Referring to Fig. 1, let us suppose that we are given the equation of the elliptic vibration described at any particular plane z in the medium. If the initial state of polarisation is to be propagated without change of form, then the equation of the vibration at the plane $z + dz$ can be obtained not only by the method of superposition but also from the usual equation for the propagation of a damped wave. By equating these two expressions we can determine not only the states of polarisation that can be propagated without change of form but also their velocities and extinction coefficients.

Let OX and OY be two arbitrary rectangular axes taken in the plane of the figure, the inclinations of OX_k and OX_r with respect to the positive x-axis being α_1 and α_2 respectively. Let the components of the arbitrary elliptic vibration P along the axes OX, OY, have the following equations (using complex notation and indicating the complex quantities by bars):

$$\left.\begin{aligned} x &= \mathrm{F}e^{i(\omega t-\theta_1)} = \bar{f}e^{i\omega t} \\ y &= \mathrm{G}e^{i(\omega t-\theta_2)} = \bar{g}e^{i\omega t} \end{aligned}\right\} \qquad (23)$$

so that

$$\frac{\bar{g}}{\bar{f}} = \frac{\mathrm{G}}{\mathrm{F}}\, e^{i\theta}$$

where $\bar{g}/\bar{f}$ is the ratio of the complex amplitudes, G/F the ratio of the real amplitudes and θ the difference of phase $(\theta_1 - \theta_2)$ between the x and y components. (It may be noted that G/F and θ will have—on the Poincaré sphere—geometrical interpretations essentially similar to those that have been described in Section 4 *c* for $\mathrm{G}_k/\mathrm{F}_k$ and θ_k.)

Let the complex amplitudes become $\bar{f}'$, $\bar{g}'$, after the infinitesimal operation of dichroism alone, and $\bar{f}''$, $\bar{g}''$, after both the infinitesimal operations of dichroism and birefringence corresponding to a passage dz. But if the initial state of polarisation $(\bar{f}, \bar{g})$ is to be propagated without change of form,

and with a specific extinction coefficient κ and refractive index n, then its state $(\bar{f}'', \bar{g}'')$ after propagating a distance dz should also be given by:

$$\bar{f}''e^{i\omega t} = \bar{f}e^{i\left(\omega t - \frac{2\pi}{\lambda_0}\bar{n}\,dz\right)}$$

or

$$\left.\begin{aligned}\bar{f}'' &= \bar{f}\left(1 - i\,\frac{2\pi}{\lambda_0}\bar{n}\,dz\right)\\ \text{and}\qquad \bar{g}'' &= \bar{g}\left(1 - i\,\frac{2\pi}{\lambda_0}\bar{n}\,dz\right)\end{aligned}\right\} \qquad (24)$$

where $\bar{n}$ is the complex refractive index $(n - i\kappa)$ of the elliptically polarised wave. We shall now, by the method of superposition, proceed to determine expressions for the final state $(\bar{f}'', \bar{g}'')$ in terms of the initial state $(\bar{f}, \bar{g})$, and then substitute these expressions in (24).

The Operation of Dichroism.—The elliptic vibration P, given by (23), is first referred to the axes OX_k, OY_k along the principal planes of absorption; the complex amplitudes $(\bar{f}_k, \bar{g}_k)$ of the components along these directions can be obtained from the amplitudes $(\bar{f}, \bar{g})$ by the usual transformation scheme for the rotation of co-ordinate axes through an angle α_1. These amplitudes $\bar{f}_k$, $\bar{g}_k$ are then multiplied by $(1 - 2\pi/\lambda_0 \cdot \kappa_1 dz)$ and $(1 - 2\pi/\lambda_0 \cdot \kappa_2 dz)$ respectively, to give the amplitudes $\bar{f}_k'$, $\bar{g}_k'$ of the x_k, y_k components after the operation of dichroism. Finally the elliptic vibration $\bar{f}_k', \bar{g}_k'$ thus obtained is referred back to the axes OX, OY; the complex amplitudes $\bar{f}', \bar{g}'$ of the components along these directions are obtained from the amplitudes $\bar{f}_k'$, $\bar{g}_k'$ by the usual transformation scheme for the rotation of the co-ordinate axes through an angle $-\alpha_1$.

If we go through the straightforward but lengthy algebraic substitutions involved in the procedure described in the last paragraph, it can be shown that the amplitudes $\bar{f}', \bar{g}'$ of the x, y components after the operation of dichroism are related to the corresponding initial amplitudes $\bar{f}, \bar{g}$ by relations which may be put in a form analogous to (24):

$$\left.\begin{aligned}\bar{f}' &= \bar{f}\left[1 - \frac{2\pi}{\lambda_0}\left(\kappa_{11} + \frac{\bar{g}}{\bar{f}}\cdot\kappa_{12}\right)dz\right]\\ \bar{g}' &= \bar{g}\left[1 - \frac{2\pi}{\lambda_0}\left(\kappa_{22} + \frac{\bar{f}}{\bar{g}}\cdot\kappa_{12}\right)dz\right]\end{aligned}\right\} \qquad (25)$$

where, if α_1 be the orientation of the positive OX_k axis,

$$\left.\begin{aligned}\kappa_{11} &= \kappa_1\cos^2\alpha_1 + \kappa_2\sin^2\alpha_1\\ \kappa_{22} &= \kappa_1\sin^2\alpha_1 + \kappa_2\cos^2\alpha_1\\ \kappa_{12} &= \tfrac{1}{2}(\kappa_1 - \kappa_2)\sin 2\alpha_1\end{aligned}\right\} \qquad (26)$$

If an ellipse be drawn with its principal semi-axes of lengths $1/\sqrt{\kappa_1}$ and $1/\sqrt{\kappa_2}$ lying along OX_k and OY_k, then $1/\sqrt{\kappa_{11}}$ and $1/\sqrt{\kappa_{22}}$ are the lengths of the radii vectors intercepted by the OX and OY directions, the equation of the ellipse being

$$\kappa_{11}\, x^2 + \kappa_{22}\, y^2 + 2\kappa_{12}\, xy = 1$$

The Operation of Birefringence.—The mathematical procedure involved in the infinitesimal operation of birefringence is essentially the same as in the operation of dichroism. The elliptic vibration $\bar{f}', \bar{g}'$ obtained after the operation of dichroism is first referred to the axes OX_r, OY_r along the principal planes of refraction; the complex amplitudes $\bar{f}_r'\, \bar{g}_r'$ of the components along these directions are then multiplied by $\exp(-i\,2\pi/\lambda_0 . n_1 dz)$ and $\exp(-i\,2\pi/\lambda_0 . n_2 dz)$ respectively—where n_1 and n_2 are the refractive indices in the absence of absorption. On referring the final vibration $(\bar{f}_r'', \bar{g}_r'')$ back to the axes OX, OY we will have the complex amplitudes $(\bar{f}'', \bar{g}'')$ of the x, y components, related to the corresponding amplitudes $\bar{f}', \bar{g}'$ (before the birefringence operation) by equations essentially similar to (25), though put in the form of (24):

$$\left.\begin{aligned} \bar{f}'' &= \bar{f}' \left[1 - i\frac{2\pi}{\lambda_0}\left(n_{11} + \frac{\bar{g}'}{\bar{f}'} \cdot n_{12}\right) dz\right] \\ \bar{g}'' &= \bar{g}' \left[1 - i\frac{2\pi}{\lambda_0}\left(n_{22} + \frac{\bar{f}'}{\bar{g}'} \cdot n_{12}\right) dz\right] \end{aligned}\right\} \tag{27}$$

Here n_{11}, n_{22} and n_{12} are to be regarded as *defined* by the relations (analogous to (26):

$$\left.\begin{aligned} n_{11} &= n_1 \cos^2 \alpha_2 + n_2 \sin^2 \alpha_2 \\ n_{22} &= n_1 \sin^2 \alpha_2 + n_2 \cos^2 \alpha_2 \\ n_{12} &= \tfrac{1}{2}(n_1 - n_2) \sin 2\alpha_2 \end{aligned}\right\} \tag{28}$$

where α_2 gives the angle made by the positive OX_r axis with the x-axis.

Since we shall omit terms involving dz^2, the value of $(\bar{g}'/\bar{f}')$ to be substituted in (27) need not include even the terms of the first order in dz, *i.e.*, we may write $(\bar{g}/\bar{f})$ for $(\bar{g}'/f')$ in (27). We then obtain as the equation connecting the final state of polarisation $\bar{f}'', \bar{g}''$ (after both the infinitesimal operation of birefringence and dichroism corresponding to a passage dz), with the initial state $\bar{f}, \bar{g}$:

$$\left.\begin{aligned} \bar{f}'' &= \bar{f}\left\{1 - i\frac{2\pi}{\lambda_0}\left[\overline{n_{11} - i\kappa_{11}} + \frac{\bar{g}}{\bar{f}} \cdot \overline{n_{12} - i\kappa_{12}}\right] dz\right\} \\ \bar{g}'' &= \bar{g}\left\{1 - i\frac{2\pi}{\lambda_0}\left[\overline{n_{22} - i\kappa_{22}} + \frac{\bar{f}}{\bar{g}} \cdot \overline{n_{12} - i\kappa_{12}}\right] dz\right\} \end{aligned}\right\} \tag{29}$$

The Final Equations for Wave Propagation.—We now introduce the values of $\bar{f}'', \bar{g}''$ given by (29), into equation (7). Conciseness will obviously be attained if we first introduce the complex quantities:

$$\bar{n}_{11} = n_{11} - i\kappa_{11}$$
$$\bar{n}_{22} = n_{22} - i\kappa_{22}$$
$$\bar{n}_{12} = n_{12} - i\kappa_{12}$$

where the n_{hk} and κ_{hk} have already been defined in relations (26) and (28). We then obtain as our final equations:

$$\left.\begin{aligned} \bar{n} - \bar{n}_{11} &= \frac{\bar{g}}{\bar{f}} \cdot \bar{n}_{12} \\ \bar{n} - \bar{n}_{22} &= \frac{\bar{f}}{\bar{g}} \cdot \bar{n}_{12} \end{aligned}\right\} \qquad (30)$$

There will be two pairs of values $(n_a, \bar{g}_a/\bar{f}_a)$ and $(\bar{n}_b, \bar{g}_b/\bar{f}_b)$ which simultaneously satisfy (30); and—since $\bar{g}/\bar{f}$ and $\bar{n}$ are both in general complex—this means that there should be two elliptically polarized waves that can be propagated, each with a specific velocity and coefficient of extinction. Eliminating $\bar{n}$ between the two equations of (30) by subtracting, we get the following quadratic in $\bar{g}/\bar{f}$ determining the states of polarisation propagated without change of form:

$$\frac{\bar{f}}{\bar{g}} - \frac{\bar{g}}{\bar{f}} = \frac{\bar{n}_{11} - \bar{n}_{22}}{\bar{n}_{12}} \qquad (31)$$

The two roots of this equation are obviously connected by the relation $(\bar{g}_a/\bar{f}_a) = -(\bar{f}_b/\bar{g}_b)$, from which it follows that the two elliptically polarised vibrations have their major axes at right angles and their ellipticities equal, but are described in the same sense (see, *e.g.*, McLaurin[9]).

Eliminating $\bar{g}/\bar{f}$ between the two equations (30) by multiplying the two, we get the following quadratic in $\bar{n}$ determining the complex refractive indices of the waves:

$$(\bar{n} - \bar{n}_{11})(\bar{n} - \bar{n}_{22}) = \bar{n}_{12}^2 \qquad (32)$$

From this we get the expressions for the sum and difference of the complex refractive indices:

$$(\bar{n}_a - \bar{n}_b)^2 = (\bar{n}_{11} - \bar{n}_{22})^2 + 4\bar{n}_{12}^2 \qquad (33)$$

and

$$(\bar{n}_a + \bar{n}_b) = \bar{n}_{11} + \bar{n}_{22} \qquad (34)$$

Velocities and Absorption Coefficients of the Waves.—The expressions for the velocities and absorption coefficients given in Section 4 may be derived from the equations (30) which give the complex refractive $\bar{n}$ in terms of the corresponding state of polarisation $\bar{g}/\bar{f}$. If we choose axes of co-ordinates along OX_τ, OY_τ then $n_{12} = 0$, $a_2 = 0$ and $a_1 = 2\chi$. The first of the two relations in (30) gives:

$$(n - i\kappa) = (n_1 - i\kappa_{11}) + \frac{G_\tau}{F_\tau} e^{i\theta_\tau} \cdot (-i\kappa_{12})$$

Equating real parts

$$\begin{aligned} n &= n_1 + (G_\tau/F_\tau)\,\kappa_{12} \sin\theta_\tau \\ &= n_1 + (G_\tau/F_\tau) \cdot \tfrac{1}{2}(\kappa_1 - \kappa_2) \sin 2\chi \sin\theta_\tau \end{aligned}$$

Referring to Fig. 2, since $\theta_\tau = PX_\tau X_k$ we have

$$\sin 2\chi \sin\theta_\tau = \sin 2\psi$$

Hence on using eq. (5), Section 4 *c*, we have

$$n = n_1 - (G_\tau/F_\tau) \cdot \tfrac{1}{2}(n_1 - n_2) \sin 2\phi$$

Since $(G_\tau/F_\tau) = \tan\phi$, we get as our final expression for the refractive index,

$$n = n_1 \cos^2\phi + n_2 \sin^2\phi$$

Similarly we will have for the extinction coefficient,

$$\kappa = \kappa_1 \cos^2\psi + \kappa_2 \sin^2\psi$$

8. Comparison with the Electromagnetic Theory

Let the sections of the index and absorption ellipsoids made by the xy plane be given by the respective equations:

$$\left.\begin{aligned} a_{11}x^2 + a_{22}y^2 + 2a_{12}xy &= 1 \\ b_{11}x^2 + b_{22}y^2 + 2b_{12}xy &= 1 \end{aligned}\right\} \tag{35}$$

Let us introduce the quantities

$$\bar{c}_{hk} = a_{hk} + ib_{hk} \tag{36}$$

Then the equations (30) giving the states of polarisation and the complex refractive indices of the two waves propagated along any direction have to

be compared with the following similar relations obtained from the electromagnetic theory:

$$\left.\begin{aligned}(\bar{v}^2 - \bar{c}_{11}) &= \frac{\bar{g}}{\bar{f}} \cdot \bar{c}_{12} \\ (\bar{v}^2 - \bar{c}_{22}) &= \frac{\bar{f}}{\bar{g}} \cdot \bar{c}_{12}\end{aligned}\right\} \tag{37}$$

where the complex velocity $\bar{v} = v(1 + ix')$

We may first remark that it would indeed be possible to *define* the quantities $\bar{n}_{11}$, $\bar{n}_{22}$ and $\bar{n}_{12}$ (in terms of $\bar{c}_{11}$, $\bar{c}_{22}$ and $\bar{c}_{12}$) in such a manner that the results obtained by the method of superposition would be identical with the results of the electromagnetic theory. But in order to retain the physical content of the method of superposition it is necessary to regard the velocities v_1 and v_2 in the absence of absorption as being equal to $\sqrt{a_1}$ and $\sqrt{a_2}$ respectively (where $1/\sqrt{a_1}$ and $1/\sqrt{a_2}$ are the lengths of the principal radii of the elliptical section of the index ellipsoid). And once this is done, at least some of the results obtained by the method of superposition have necessarily to be regarded as approximations. We shall however show that for directions near an optic axis where the birefringence is necessarily very small and where alone the ellipticity of the waves play an important role, the error involved is negligible. To this end we shall start by assuming the relations (12) and (14) which give a connection between the extinction coefficients κ_1 and κ_2 on the one hand, and the lengths $1/\sqrt{b_1}$ and $1/\sqrt{b_2}$ of the principal radii of the elliptical section of the absorption ellipsoid on the other. The quantities a_{hk} occurring in equation (35) can obviously be expressed in terms of a_1 and a_2 thus:

$$\left.\begin{aligned}a_{11} &= a_1 \cos^2 \alpha_2 + a_2 \sin^2 \alpha_2 \\ a_{22} &= a_1 \sin^2 \alpha_2 + a_2 \cos^2 \alpha_2 \\ a_{12} &= \tfrac{1}{2}(a_1 - a_2) \sin 2\alpha_2\end{aligned}\right\} \tag{38}$$

Similar relations analogous to (26) hold for the b_{hk}.

On examining the equations [(30) and 37)] obtained by the method of superposition and by the electromagnetic theory, we notice that the two are entirely similar in form, the only difference being the occurrence of the quantities $\bar{c}_{hk}$ instead of $\bar{n}_{hk}$ and $\bar{v}^2$ instead of $\bar{n}$. Hence it follows that given any equation obtained by the method of superposition, a corresponding exact equation obtainable from the electromagnetic theory can be written down, merely by changing the symbols occurring in the equation according to the following scheme:

n	n_1	n_2	κ	κ_1	κ_2
v^2	a_1	a_2	$-\frac{2\kappa v^3}{c}$	$-b_1$	$-b_2$

Thus to obtain the states of polarisation (ϕ, ψ) that can be propagated without change of form, we have to replace the ratio δ/k in eqn. (5) by the ratio ρ/σ where $\rho = \frac{1}{2}(a_2 - a_1)$ and $\sigma = \frac{1}{2}(b_2 - b_1)$. This replacement will however leave the equation unaltered, as we have already shown in Section 4 (*d*) that $\delta/k = \rho/\sigma$. It is also possible to show that the *sense* of description of the two vibrations as obtained by the method of superposition is the same as that obtained by the electromagnetic theory.

Expressions for the velocities and absorption coefficients according to the electromagnetic theory may be similarly written down from the relations (15) and (16):

$$v^2 = a_1 \cos^2 \phi + a_2 \sin^2 \phi \tag{39}$$

$$\frac{2\kappa v^3}{c} = b_1 \cos^2 \psi + b_2 \sin^2 \psi \tag{40}$$

We hence obtain

$$(v_a{}^2 - v_b{}^2) = (a_1 - a_2) \cos 2\phi_a$$

Or, if v_m be the mean velocity introduced in Section 4 (*d*)

$$\frac{v_b{}^2 - v_a{}^2}{2v_m{}^3} \cdot c = (n_1 - n_2) \cos 2\phi_a$$

On comparing this with the last equation in (16) we see that the approximation involved in using the method of superposition is to regard the expression on the left-hand side of the above equation as being practically equal to the difference in refractive indices $(n_a - n_b)$. This is justifiable along directions where the birefringence is low, and in fact this same approximation is also made when the propagation in transparent optically active crystals is regarded from the standpoint of superposition (Pockels, *loc. cit.*, p. 312).

From Eqn. (40) we get

$$2\kappa_a v_a{}^3 - 2\kappa_b v_b{}^3 = (b_1 - b_2) \cos 2\psi_a$$

Or, using (12)

$$\frac{\kappa_a v_a{}^3 - \kappa_b v_b{}^3}{v_m{}^3} = (\kappa_1 - \kappa_2) \cos 2\psi_a$$

On comparing this with the last equation in (15), we see that the approximation we have to make is to regard the expression on the left as being prac-

tically equal to the difference in extinction coefficients ($\kappa_a - \kappa_b$)—an approximation that is again justifiable where the birefringence is low.

It may be similarly shown that the mean refractive index and the mean extinction coefficient are also only negligibly in error. We shall not however give the proof here since the absolute values of the velocities and extinction coefficients are not as important as their *differences.*

The author wishes to express his thanks to Professor Sir C. V. Raman for his kind interest in this work.

9. Summary

The optical behaviour of pleochroic biaxial crystals in the vicinity of an optic axis can be elegantly interpreted as due to the effects of linear birefringence and linear dichroism superposed continuously along the depth of the material. This idea—followed up geometrically with the Poincaré sphere, and analytically by direct algebraic methods—explains the *elliptical* polarisation of the two waves propagated in any general direction, as due to the non-coincidence of the principal planes for the usual operation of birefringence with those for the operation of dichroism. In particular, it also explains the existence, on either side of an optic axis, of two *singular axes*—along any one of which *only one* circular vibration with a definite sense of description can be propagated unchanged: for these directions the principal planes of absorption and refraction make angles of 45° with each other, the linear birefringence and dichroism being also equal in magnitude.

A discussion is also given of the effects to be expected when a circular vibration incident in the direction of a singular axis has a sense of description *opposite* to that which can be propagated unchanged; and it is shown that—contrary to what Voigt expected—the emergent intensity will not be either zero or negligible, but will in fact be *greater* than when the sense of description of the incident vibration is reversed.

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